

CHEMICAL EDUCATION

Published by the DIVISION OF CHEMICAL EDUCATION OF THE AMERICAN CHEMICAL SOCIETY

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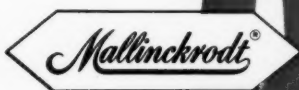
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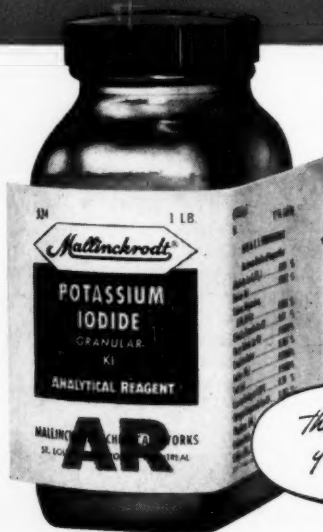
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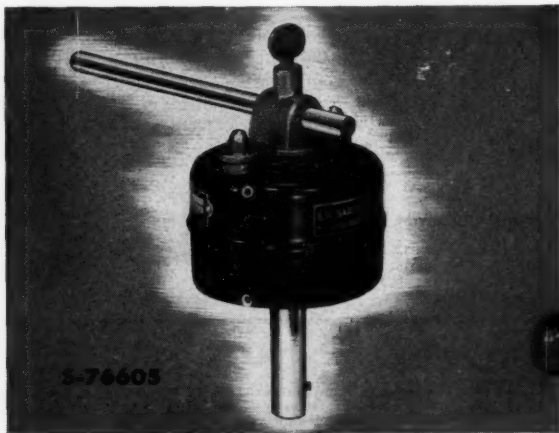
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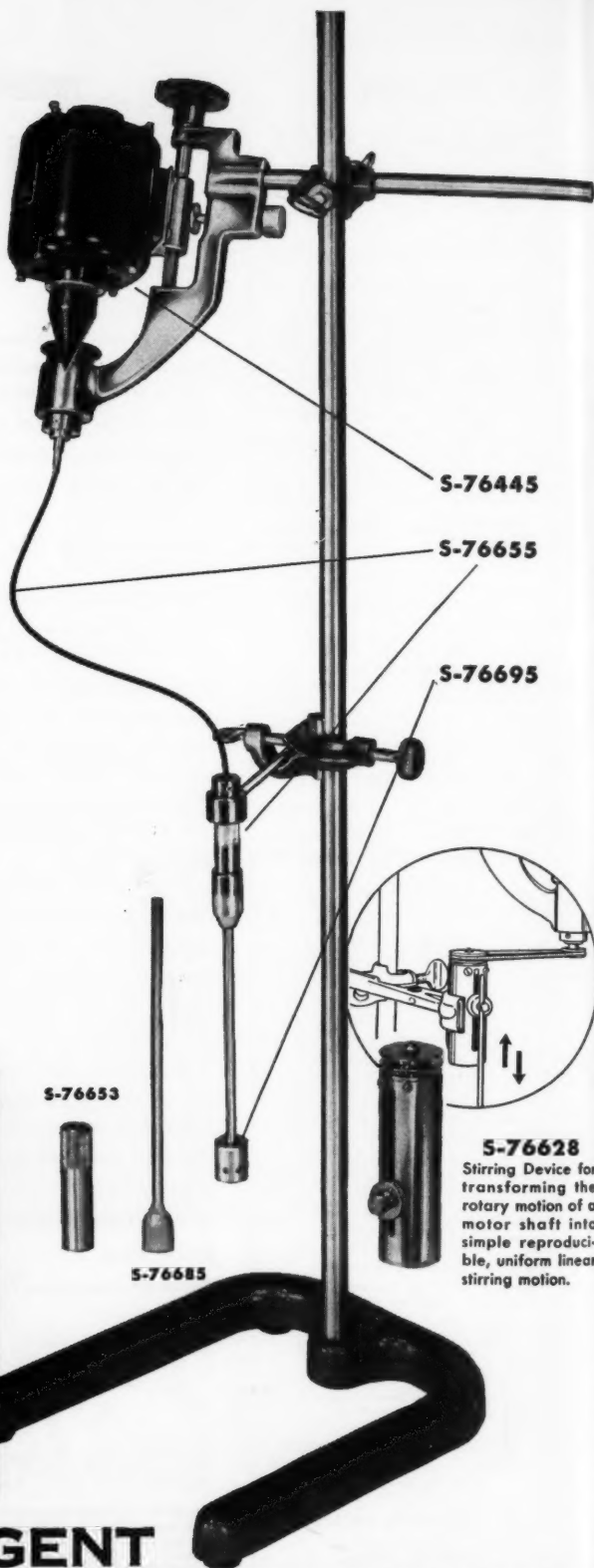
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9. ATOMIC STRUCTURE. RADIOACTIVITY

A. GENERAL

- *9-1 **Exhibit:** atomic and molecular models, models of nuclei of isotopes; crystals, minerals and models illustrating crystalline forms.

B. NUCLEAR PHENOMENA: ISOTOPES

- 9-2 Perform 3-18 showing that the freezing points of H₂O and D-O differ.
- 9-3 See F. J. Norton, *J. Chem. Educ.* 25, 677 (1948) and J. Fernandez and S. H. Lebowitz, *ibid.* 26, 334(1949). Apparatus demonstrating the principle of the mass spectrograph. **Demonstrate.**

C. NUCLEAR PHENOMENA: RADIOACTIVITY

Historical

- 9-4 *Becquerel's discovery.* **Exhibit:** photographic plate wrapped in black paper, key, lump of uranium ore, self-photograph made by a lump of radioactive ore.
- 9-5 *Electroscope.* Hard-rubber rod, cat's fur, radioactive source, electroscope arranged so a shadow of the gold-leaf electrodes can be projected on a screen. **Charge the electroscope, then show discharge with a radioactive source.**
- 9-6 Roentgen rays. *Exhibit X-ray tube.*

Fog-Track Phenomena

- 9-7 *Formation of Fog.* A 3-way stopcock, with one arm leading through rubber stopper into a 1-liter round-bottom distilling flask brightly illuminated, with side-arm leading to water aspirator or vacuum pump. Second arm of stopcock leading to the air; the third arm leading to a tubing 15 mm X 30 cms. packed loosely with cotton. Place about 100 ml. water in the flask. **Suck air through the flask, then suddenly turn stopcock to evacuate: a fog forms. If flask is first filled with air filtered by sucking it through cotton for 10 minutes, no fog is produced upon sudden evacuation.**
- 9-8 Commercial cloud chamber: **exhibit.**
- *9-9 *A simple cloud chamber.* Glue a circle of black felt inside the cap of a glass jar 3" high and 3" in diameter (Skippy Peanut-butter jar). Glue another felt to the inside bottom of the jar. Saturate both felts with methyl alcohol, screw on the top, invert jar on a block of dry ice, and shoot a spotlight diagonally through the side of the jar, so that it enters the jar near the top and emerges near the bottom. **Cloud tracks due to cosmic rays will be seen in about 15 minutes, after thermal equilibrium has been established in the jar. If a gamma**

source is brought to the side of the jar, many fog-tracks will be seen inside the jar.

Fluorescence Phenomena

- 9-10 High voltage discharge tube set up with fluorescent tubes, ultra-violet light, fluorescent paints, fluorescent lights. **Show UV light causes paints to fluoresce. Light fluorescent lights. Turn on high-voltage discharge tube, showing fluorescence from beta ray (electron) bombardment.**
- *9-11 **Exhibit:** Crookes spinthariscopes.

Intensity measurements

- *9-12 *Absorption of beta rays.* Beta source (uranyl nitrate), Geiger counter, count-rate meter, beta source, sheets of paper, Al foil, Pb foil, Al sheet, Pb sheet, book. **Adjust amount of radioactive source so as to get 1000 counts per minute with the probe 6" away. Successively interpose foils, sheets and book, and record new counts.**
- 9-13 *Thickness measurements, by beta ray count.* Geiger counter, count-rate meter, beta source (RaD and RaE source metal plaque, National Bureau of Standards), rubber inner tube from an automobile tire. **Interpose a sheet of inner tube between the beta**

Turn the page for additional demonstrations

*Footnotes

- 9-1 See F. L. Lambert, *J. Chem. Educ.* 30, 503(1953) for use of poly-styrene balls for constructing molecular models.
- 9-9 This apparatus is best set up so the students can examine it during the laboratory period.
- 9-11 The scintillations of the ZnS screen in the Crookes spinthariscopes can only be seen if the student remains in the dark many minutes before using the instrument. Although it obviously does not lend itself to lecture demonstration, it should be exhibited in lecture since it was so powerful a tool in early nuclear research, for instance in Rutherford's use of it in bombarding air, N₂, and O₂ with alpha particles and counting scintillations in his first man-made transmutation studies.
- 9-12 Experiments 9-12 through 9-18, and other interesting experiments using a Geiger counter, are described in *Laboratory Experiments with Radioisotopes for High School Science Demonstrations*, edited by Samuel Schenberg for the Atomic Energy Commission, August, 1953, and obtainable from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.; price 30 cents.
- Labels for Topic 9. (For code, see instructions for assembling kits, *J. Chem. Educ.*, 32, 12A(1955).) 9-4-w-uranium ore, 9-5-J-cat's fur, 9-5-J-hard-rubber rod or comb, 9-7-J-cotton, 9-9-N-methyl alcohol, 9-12-J-Al foil, 9-12-J-Pb foil, 9-12-J-Al sheet, 9-12-J-Pb sheet, 9-13-J-piece of rubber inner tube, 9-14-J-cylinder of Al, 5 cm. dia. X 15 cms. high, 9-14-J-cylinder of paper, 9-14-J-cylinder of Pb, 9-20-w with shaker top-NaCl, 9-20-w with shaker top-CuCl₂, 9-20-w with shaker top-SrCl₂, 9-20-w with shaker top-BaCl₂, 9-21-J-fluorescent minerals, 9-26-w-Mg ribbon, 9-26-w-granular Al, 9-26-J-rubber balloons, 9-26-J-string, 9-27-w-CCl₄, 9-27-w-ethyl alcohol, 9-27-w-sugar aq., 9-27-w-NiCl₂ aq., 9-27-w-CuSO₄ aq., 9-27-w-K₂Cr₂O₇ aq., 9-28-N-CuSO₄ aq., 9-28-N-NH₄OH.

source and the probe. Stretch the sheet to twice its length (half its thickness) and record change in counts.

- 9-14 *Scattering of beta rays.* Geiger counter with probe, count-rate meter, radioactive beta source (uranyl nitrate in petri dish), hollow cylinders 5 cm. dia. \times 15 cms. high, of Al, Pb and paper. Place a cylinder over radioactive source. Lower probe into cylinder, contrast counts, as the walls of the cylinders act in reflecting beta rays. Sample counts: 1150, 500, 300, and 70 for Pb, Al, paper, and no cylinder respectively.
- 9-15 *Gamma ray: inverse square law.* Gamma source (such as I-131), Geiger counter, count-rate meter, meter stick. Record number of counts as probe is moved to fixed positions away from the radioactive source. Be sure to hold the gridded side of the counter, not the closed end, towards the radioactive source. Graph results on the board.
- 9-16 *Absorption of gamma rays.* Geiger counter, count-rate meter, five $4 \times 4 \times \frac{1}{32}$ " lead plates, gamma source. Fix the probe at that distance from the radioactive source which gives about 1000 counts per minute. Record counts as an increasing number of lead plates is interposed between the probe and the radioactive source.

Effects of rays

- 9-17 *Chemical effects.* Radium needle, 500 ml. bulb with a bulb the size of a pinhead mounted in its center. Explain how pinhead bulb is filled with radon, the alpha particles from which penetrate the extremely thin glass and cause ionization, and subsequent chemical reaction, of reactants in the surrounding larger bulb. Explain action of radium needle obtainable from local hospital.
- 9-18 *Botanical effects: translocation of phosphorus in plants.* Geiger counter, count-rate meter. Immerse a young tomato plant, 6" high, in beaker of water containing 10 millicuries of radioactive P-32 in the form of Na_2PO_4 . Wrap beaker and all but the leaves of the plant in a shield of lead foil. Measure the radioactive count at 10 minute intervals for (a) the lower leaves and (b) the upper leaves. The count will increase noticeably during the lecture hour.

D. NUCLEAR PHENOMENA: ARTIFICIAL TRANSMUTATION

- 9-19 *Exhibit:* Model of atomic pile (nuclear reactor), sample of uranium and its ores,

radiation badges and other items used in radiation studies. Discuss operation of nuclear reactor, cyclotron, etc.

E. PLANETARY PHENOMENA

Structure

- 9-20 Salt shakers containing chlorides of Na, Cu, Sr, Ba; burner, spectroscope. Shake salts into flame to show flame tests.
- 9-21 Sodium lamp, neon light, mercury lamp; fluorescent minerals, paints, lamps. Demonstrate fluorescence; light the lamps.
- 9-22 Photocell set up to operate a relay, which in turn will ring a bell or light a lamp bulb. (a) Shine flashlight on photocell, to ring bell. (b) Light a match near photocell, so as to light the electric lamp bulb then blow out the match, which "blows out" the lighted lamp. (c) Light the lamp again, but this time bring it around so that it shines on the photocell. This is apparently perpetual motion, because the light from the lamp bulb operates the photocell, which closes the relay, which turns on the light bulb, and so on!
- 9-23 *Exhibit:* models and charts of planetary structures of the elements.
- 9-24 *Exhibit:* X-ray tube, charts showing X-ray lines. Explain the X-rays originate when electrons return to the lowest planetary level, the method for measuring atomic numbers.

Formation of compounds

- 9-25 *Exhibit:* models illustrating types of binding in matter.
- 9-26 *Electrovalent bonds.* Rubber balloon containing 23 mg. Na fastened tightly over mouth of 100 ml. bottle of water. Similarly 24 mg. Mg over HCl-aq., and 27 mg. Al over HCl-aq. Dump the metals into the liquids; show 1, 2 and 3 volumes of H_2 generated, corresponding to Na^+ , Mg^{++} and Al^{+++} .
- 9-27 *Covalent bonds.* Use apparatus from experiment 6-2. CCl_4 , ethyl alcohol, sugar-aq., NiCl_2 -aq., CuSO_4 -aq., $\text{K}_2\text{Cr}_2\text{O}_7$. Show conductivity of salt solutions, non-conductivity of the organic substances.
- 9-28 *Coordinate covalent bonds.* CuSO_4 -aq., NH_4OH , 1000 ml. beaker, stirring rod. Add NH_4OH forming pale blue $\text{Cu}(\text{OH})_2$ precipitate, and eventually soluble deep-purple tetra-ammine cupric sulfate. Explain how the NH_3 is linked to the Cu^{++} by coordinate covalent bonds.

Next month's Tested Demonstrations in General Chemistry

10. GROUP ZERO (INERT GASES) AND THE ATMOSPHERE

For a complete list of topics for 1955-6 see J. Chem. Educ., 32, 28-9(1955)

Out of the Editor's Basket



Coulometric Titrator

A new coulometric titrator, automatic in operation and designed especially for the determination of mercaptan sulfur content in petroleum stocks and other organic liquids, has been developed by the Standard Oil Co. (Indiana). Manufacture and sale of the instrument will be handled under exclusive license agreement by Central Scientific Co., 1700 Irving Park Rd., Chicago, Illinois.

Micromanipulator

The "Hilleman Micromanipulator" is now offered by Custom Scientific Instruments, Inc., 541 Devon Street, Kearny, New Jersey. The unit was designed and developed by Dr. Howard H. Hilleman, School of Science, Oregon State College, Corvallis, Oregon. This micromanipulator has the following features:

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Dial-reading Calipers

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scales or graduations on a micrometer sleeve. The dials indicate 1/1000 of an inch or 1/10 mm (1/20 mm can be easily estimated).

Viscometer

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Ammonia Leaks Test Paper

A new pocket-size device for detecting ammonia leaks is being offered to ammonia users by Nitrogen Division, Allied Chemical & Dye Corporation.

The device is a booklet containing paper strips impregnated with phenolphthalein. By tearing a strip from the book, saturating it with water and holding it near suspected leaks, the user can detect the presence of ammonia when the color of the paper turns red.

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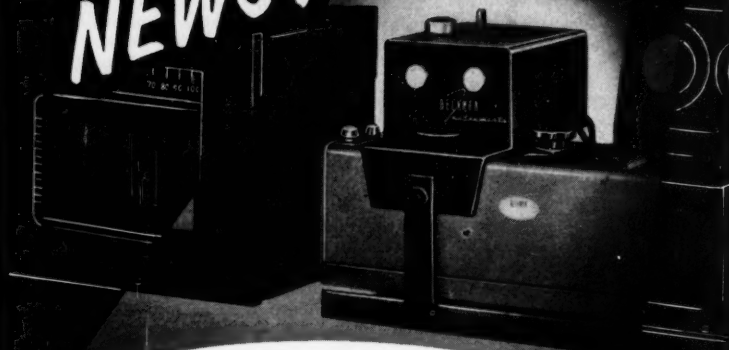
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Other articles in the JOURNAL, which are most often referred to by commentators, are its reviews of industrial processes and practices, and its historical and biographical sketches. Abstracts, book reviews and extended discussions of subjects impossible to include in textbooks are regular features.

These articles are clear, concise and authoritative. They are varied in topic and sufficiently non-technical to be of general value. They form a living textbook of chemistry—an invaluable source of material not to be found in reference volumes, or elsewhere.

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EASTON, PENNSYLVANIA

the attainment of high vacuum without resorting to traps involving liquid air or charcoal. It is chemically and thermally stable, within the limits imposed by high-vacuum pump utilization.

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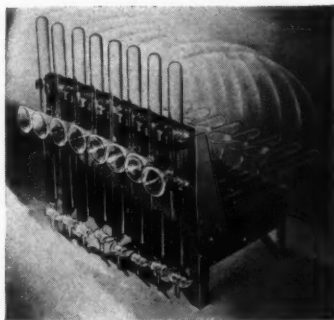
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Blue M's Unique Magni-Whirl feature now incorporated into a series of new baths for general laboratory and hospital use and for specific A.S.T.M. tests.

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Automatic Separatory Funnel

E. Machlett & Son has announced an automatic separatory funnel which—according to the Company—takes the "work" out of making extractions and yields faster, more complete, results.



Called the VirTis Extracto-Matic, the apparatus was developed by Dr. E. M. Nadel and F. Highhouse at the National Institute of Health. Extracto-Matic—made of stainless steel—consists of a compact box type stand which houses a heavy-duty 110 volt, a. c. motor. Clamps mounted on a sturdy rocker arm firmly hold eight specially designed "Pyrex" separatory funnels. Thus, up to eight extractions can be performed at one time. Prices, delivery data and answers to all questions regarding Extracto-Matic will be supplied by E. Machlett & Son, 220 East 23rd Street, New York 10, New York.

Laboratory Model Turba-Film Evaporator

A portable, laboratory model Turba-Film Evaporator for pilot plant study of the unit operations of evaporation, single step distillation, deodorization, heating, cooling, or other heat treatment,

is now available from Rodney Hunt Machine Co., Orange, Massachusetts. The evaporator uses Rodney Hunt's unique agitated film method and is provided with a heat transfer area of one square foot.

Rodney Hunt's evaporator is designed to handle organic and inorganic chemicals, solvents, latices, pharmaceutical "mycins," vitamins, juice concentrates, edible oils, gelatine, glues, confectionaries, coffee, and detergents.

Water Hardness Test Kit

The hardness of water delivered by home or industrial water softeners can now be measured to the nearest 0.2 grain per gallon in an on-the-spot test that takes only one minute.
A new pocket-size "Zeo-Kit" announced

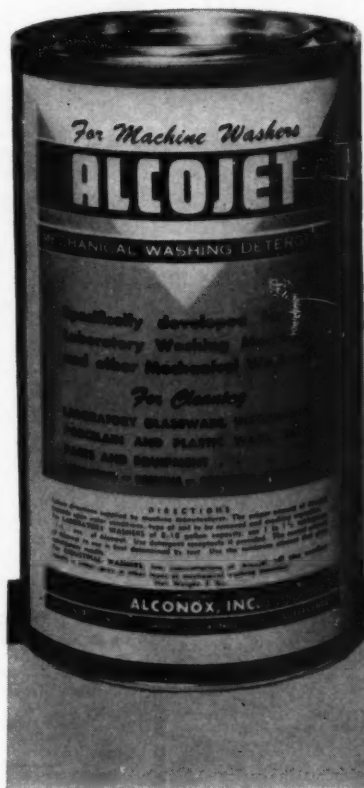
by Calgon, Inc., 323 Fourth Avenue, Pittsburgh 30, Pennsylvania, enables quick determination of when the softeners need regenerating.

Contained in a white plastic box that measures 4 3/8" by 1 3/4" by 1", the three-ounce kit consists of a glass vial and a dropper bottle holding one ounce of softener reagent. The one ounce of reagent is sufficient to make 140 tests on water averaging 0.5 grain per gallon.

NEW LITERATURE

● *Brine for Today's Industry* is the title of a new booklet on the Lixate Process just published by the International Salt Company. This 32-page booklet replaces *The Lixate Process for Making Brine* that has been a standard reference for brine users for many years. The new

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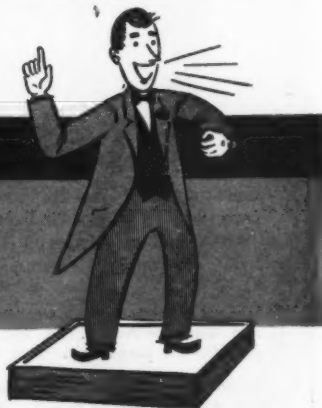
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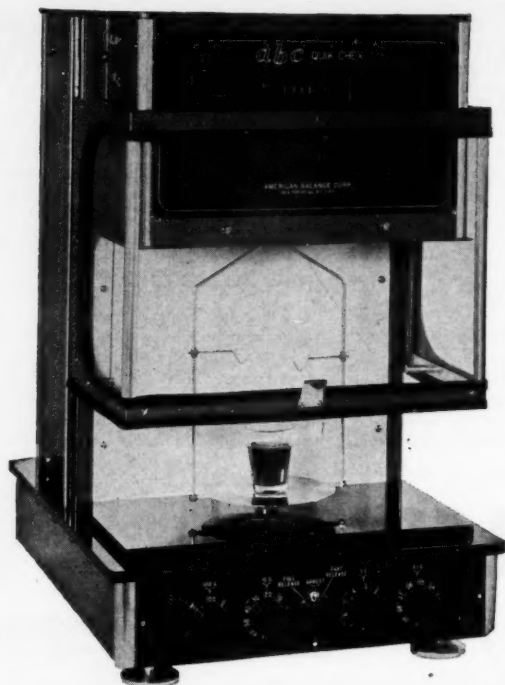
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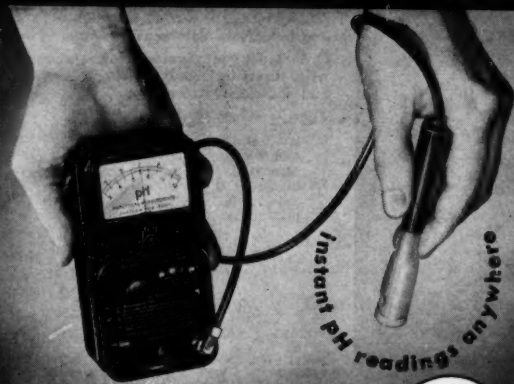
Descriptive bulletin QC gives complete specifications. Write for a copy.

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booklet contains a good deal more technical information than its predecessor and should prove to be even more helpful to industrial brine users.

● The United States Testing Company, Hoboken, New Jersey, announces publication of a new booklet entitled *Selected Scientific and Engineering Tables and Data*. Issued in commemoration of the company's 75th anniversary, the booklet is composed of many kinds and types of technical information, reflecting the many fields of activity of this diverse testing organization.

The material contained in *Tables & Data* is unique in its compilation. This 112-page paper-bound volume contains selected Chemical and Physical, Engineering, Plastics, Bacteriological, Leather, Psychometric and Textile tables and charts, arranged for easy reference.

Interested individuals may obtain a copy by writing on their company or institution letterhead to H. M. Block, Vice President, at the Hoboken, New Jersey laboratory.

● *Summer Stock* is the name of a new publication recently introduced by Schaar and Company. It serves as a summer replacement for the regular publication, *Lab-ORATORY*, and features a revue of new equipment and apparatus for industrial, educational and institutional laboratories. Write for your copy to Schaar and Co., 754 W. Lexington Street, Chicago 7, Illinois.

● A new data sheet on the Cine-Kodak and Kodak High Speed Infrared Film has been prepared by the Eastman Kodak Company and is now ready for distribution.

The film has found extensive applications in medical, scientific, documentary, legal and industrial photography, and in photomicrography. An idea of the high speed of this new film is gained from its tungsten exposure index with Wratten A filter, of 160.

Copies of the data sheet are available without charge from the Sales Service Division, Eastman Kodak Company, Rochester 4, New York.

● *Colloids Out of the Sea* is a new brochure which describes some of the interesting uses for SeaKem Colloids—in ice cream, puddings, chocolate milk, toothpaste, and other food, drug, cosmetic, pharmaceutical and industrial products.

Listed on the center spread of the brochure is a concise summary of various stabilizing functions for which SeaKem Colloids are used . . . and a picture sequence on the following page shows how this "modern product of modern processing techniques" is derived from the basic source material, Irish Moss.

You may secure copies of this new brochure by writing Mr. Byron Spence, Vice President in Charge of Sales, Seaplant Chemical Corporation, 63 David Street, New Bedford, Massachusetts.

● Arthur H. Thomas Company, Philadelphia, Pennsylvania, announces publication of a 264-page Supplement to their 1472-page general catalogue. Sturdily bound and fully indexed, the

(Continued on page 32)

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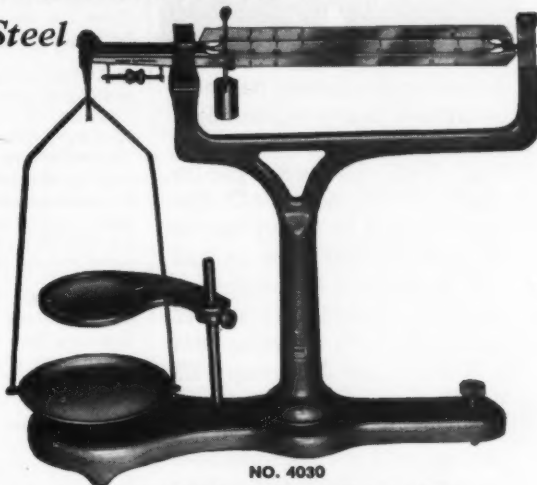
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NEWS from FILTERTOWN

A recent survey establishes that clarity of filtration is the most important factor in the selection of a filter medium. Since *E&D* filter papers give the "finest" filtration, more *E&D* filter papers are used by industry than the total of all other filter papers combined . . . To cite but a few applications: grades 609 (WINE-BRITE) and 902 (*BREW-BRITE®) are widely used in filtration of alcoholic beverages; 623 is extensively used for filtration of chemicals; 615 and 617 for foods and beverages; 613 for drugs and toilet preparations; and there are many more . . . This is not to say that any grade is universally used in any specific industry. Too many varying factors make this impossible. That is why *E&D*'s know-how, based on the practical experience of many decades, enables us to help you select the right grade for your particular assignment . . . Moreover, this is the only company in America exclusively engaged in the manufacture of filter paper for science and industry. There are many regular grades and special grades available. You can rely on any *E&D* filter paper to perform as recommended. Why take a chance on unidentified papers? The cost in loss of time and money can be serious . . . Write for free samples. Test them. Discover why *E&D* filter papers are used exclusively by most of America's leading industries . . . If you have a bothersome filtration problem write for our free Filtration Analysis Report. Chances are we know the answer . . . Used alone, or with cloth, there's an *E&D* filter paper to give you clarity of filtration and savings in time, labor and money.



(Continued from page 31)

Supplement follows the tradition of the catalogue and provides factual, detailed, and up-to-date listings of items added to their stock since publication of the catalogue in 1950. Also included is a Price List covering all current items in both catalogue and supplement.

● A four-page, two-color bulletin describing its glass capillary tubes has been published by Friedrich & Dimmock, Inc., Lincoln Avenue, Millville, New Jersey. The tubes are commonly used for containing smallpox and other vaccines; for determining blood coagulation time rates; boiling points and melting points; for providing wide bearings for moving parts and for electronic components.

● A portable constant temperature circulator, which, according to the manufacturers has been lab-tested for over 5,000 hours of continuous operation and 8,000 hours of intermittent, is described in a 4-page brochure which includes X-ray diagram, in-use photo, description, and price data. Photos and prices of immersion heater, relay, and thermostat with thermometer are also shown. Bulletin is available from Bronwill Scientific, P.O. Box 127, Rochester, New York.

● Multiple pressure readout systems to speed up data handling for process industries, wind tunnels, engine test facilities, and marine model basins are illustrated in color in Fischer & Porter Company's new 12-page catalogue 58-15. It is available on request from Fischer & Porter Co., 393 Jacksonville Rd., Hatboro, Pennsylvania.

● The typical properties, applications and compatibility characteristics of Eastman's new polyethylene waxes. Epolene "E" and Epolene "N," are described in effective detail in a new eight-page booklet just issued by Eastman Chemical Products, Inc., of Kingsport, Tennessee.

● A four-page bulletin describing Beckman's new automatic infrared spectrophotometer is just off the press. The Model IR-2A described is a high-performance, low-cost instrument suited to both research and quantitative analysis. With emphasis on performance, the bulletin gives full specifications and exact reproductions of the transmittance type curves produced by the IR-2A. Included is the spectrum of polystyrene, an accepted test for infrared instruments.

For copies write Beckman Division, Beckman Instruments, Inc., Fullerton, California. Request Bulletin 410.

● Data sheet describes batch and continuous models of laboratory Flash-Evaporator for quickly separating solvents from solutes. For copies, write to Arthur S. LaPine & Company, 6001 South Knox Ave., Chicago 29, Illinois.

● A folder describing their laboratory demineralizer is available from Scientific Equipment Corporation, 5438 Lowell Avenue, Indianapolis 19, Indiana. The unit is illustrated and its 11 features are

(Continued on page 35)

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All your laboratory needs can be taken care of quickly, at lowest cost when you buy Precision equipment. Over 1500 items are available from Precision to meet your every requirement.

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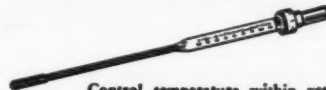
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Precision Scientific Company

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Chicago 47

described. Prices are given both for the demineralizer and the cartridges.

MISCELLANY

★ The announcement of superior chemicals for stabilization processing of oscillograph, electrocardiograph and seismographic recording materials is made by the Photo Concentrates, Inc., of Peekskill, New York.

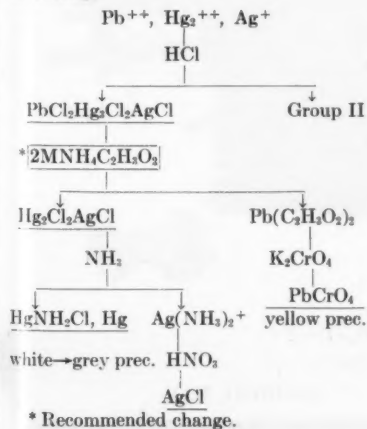
The chemicals are liquid concentrates and merely require the addition of water, thus eliminating the usual labor of mixing incurred with powdered chemicals.

★ Two new Univac-Scientific models have been announced by Remington Rand Inc., incorporating developments making this electronic computer compatible with the company's commercial Univac, and the recently announced File-Computer.

The new development which makes it possible for these computers to work together is the input-output medium, the metal magnetic tape. Previously, the Univac-Scientific operated with a plastic tape which could not be used with the other models. Now, the metal magnetic tape makes it possible for installations utilizing any two or all three of these computers to feed data and results from one to the other interchangeably, representing a big step forward in the integration of electronic data processing methods.

The Univac-Scientific can now utilize the auxiliary equipment developed for the commercial Univac. Of major interest in this connection is the High-Speed Printer, which prints results of computations and data reduction at a speed of 600 lines per minute, in any desired format. This and other equipment which can now be used with Univac-Scientific further increase its value to users.

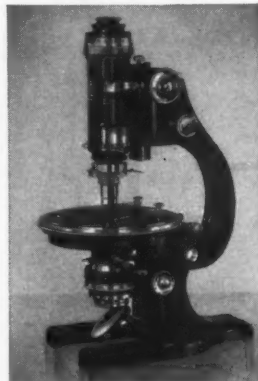
★ Professor Janis Dillaha and Frank S. Caruso of Colby College suggested the use of ammonium acetate in the separation of lead in Group I of the qualitative scheme. They have found that the use of hot 3-molar ammonium acetate in place of hot water, as shown in the diagram, separates lead more completely from the mercurous and silver ions. This prevents confusion in the identification of mercury. The separation may safely be carried out by centrifugation since the soluble lead acetate formed remains soluble on cooling.



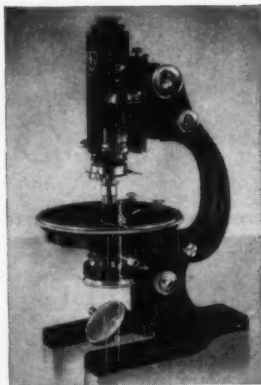
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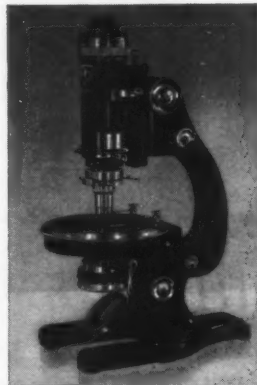
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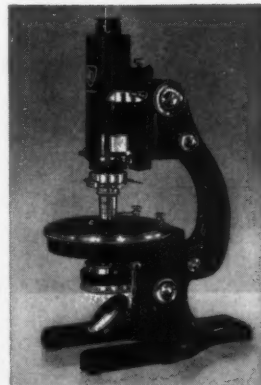
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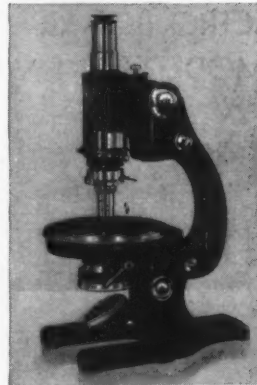
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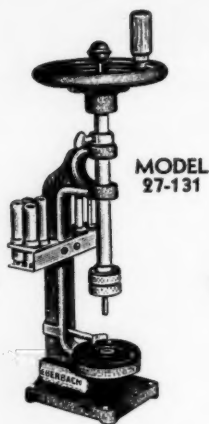
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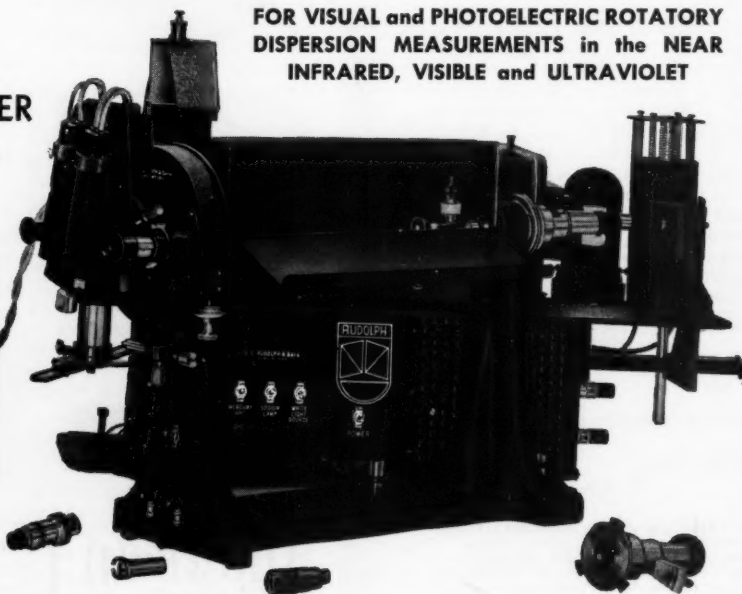
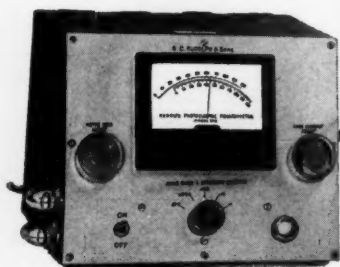
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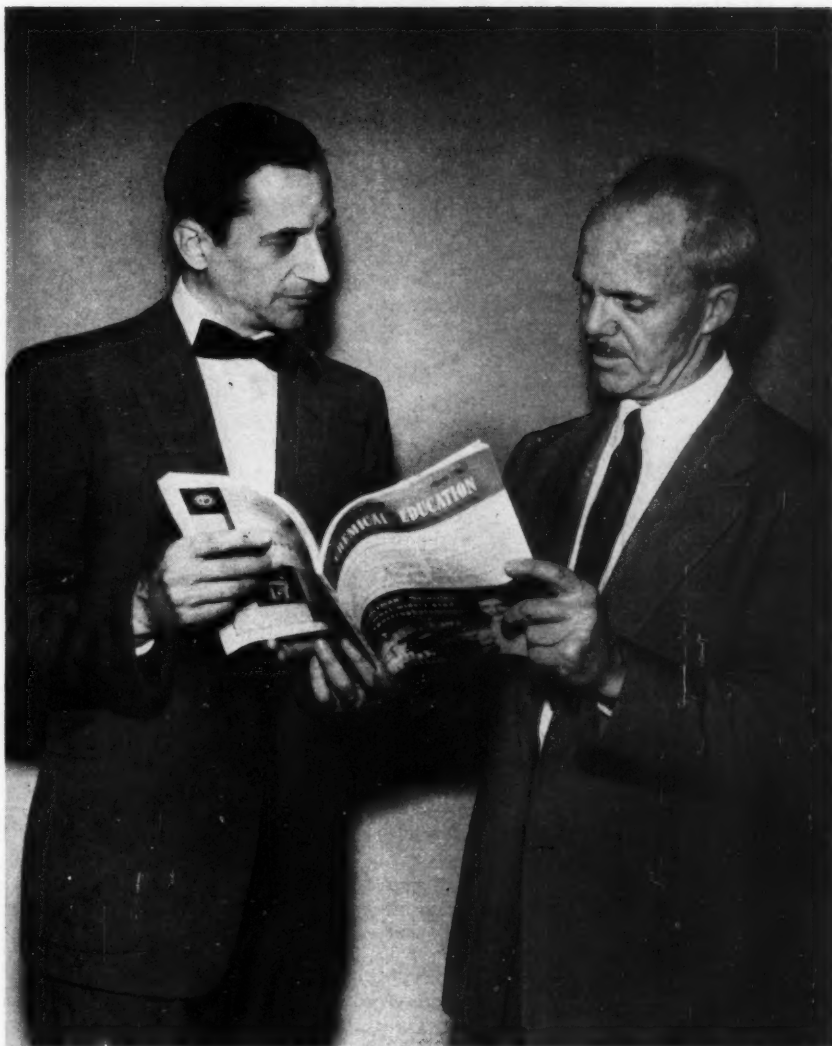
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Chem. Eng. News

Editorial Office Changes Hands

Norris W. Rakestraw (Right)

William F. Kieffer (Left)

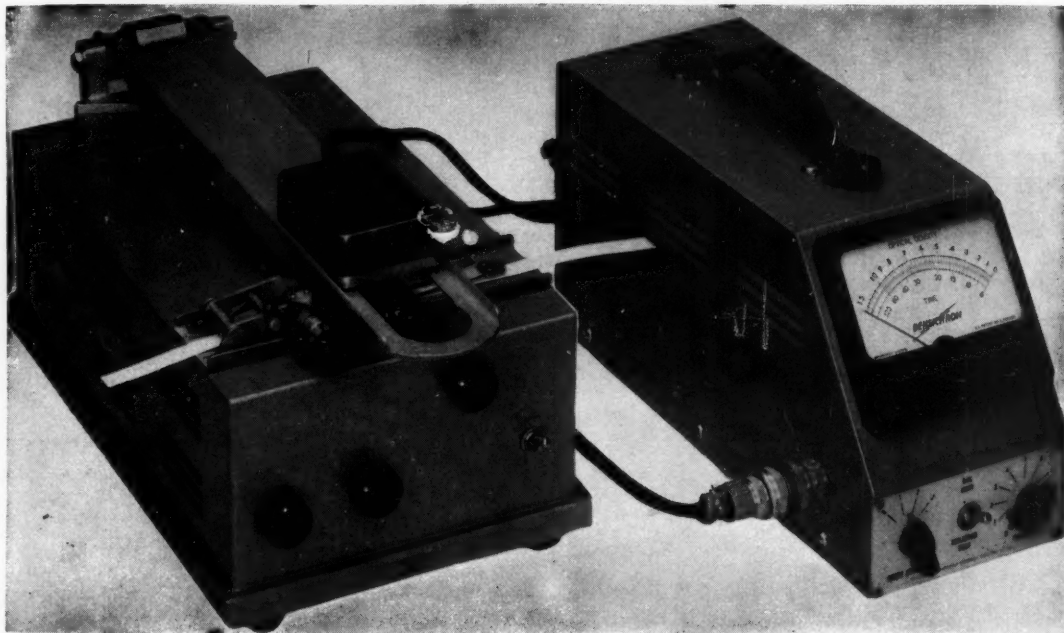
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It has been found that, because of the differential migration of the solutes through filter paper the maximum color density of the paper is proportional to the concentration of material. The "no drift" feature and the high sensitivity of the Densichron provide measurements of excellent repeatability with accuracies having high statistical significance. It has been successfully used for amino acids, sugars, vitamins, steroids, hormones, drugs, and an endless variety of both organic and inorganic compounds.

Write for literature describing the production of papergrams and the use of the Densichron for quantitative determination by the maximum density method.

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DENSICHRON WITH BLUE OR RED PROBE. This consists of the amplifier with logarithmic-scale meter, blue or red sensitive probe, metal probe support, five different measuring apertures, a cone with $\frac{1}{8}$ -inch aperture, and a set of instructions. The amplifier operates on 115 volts, 60-cycle A.C., only, except on special order.

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Editor's Outlook

FIFTEEN years ago this month I wrote in this column:

Undertaking the Editorship of the JOURNAL OF CHEMICAL EDUCATION is at the same time a responsibility and a challenge. Probably everyone who has inherited the administration of a "going concern" like this has the same mixture of feelings; a desire to conserve safely the gains of the past, enlivened by the optimistic thought that perhaps a good thing can be made even better. Two sound and successful editorial terms have preceded this one, and we only hope that when we, in our turn, hand over the shears and wastebasket to our successor we can do so with as much pride in our own accomplishment as can justly be felt by our two predecessors.

After such a long period as 15 years, everyone (whether an editor or not) owes it to himself and to his associates to stop and take stock of things. So, what about the implications in the paragraph above; to what extent have they been realized?

First, I have learned the futility of the editorial "we." How editors ever got into the habit of dividing their responsibility among a fictitious plurality I do not know. What a cowardly lot they must be! Why cannot one come right out and say: "I did this. . . . It is *my* opinion. . . ." Nevertheless, from here on, I too shall be using "we," not editorially but collectively. The responsibility for the present status of THIS JOURNAL is not the editor's alone, but is shared by many people who have helped to make it what it is, by reading manuscripts, by reviewing books, by doing the many things that must be done but which the editor cannot do himself. What state of affairs have *we* brought about?

In 1940 the JOURNAL was still "in the red," although it was beginning to make progress against the flood. We have since not only paid off our debts but have accumulated a decent little surplus which is laid away against the possibility of another series of rainy days like those of the 1930's.

We have almost doubled our circulation. I would like to think that this reflects an improvement in the editorial content, but there is danger of too readily assuming too much in this regard. It is doubtless also the result of more active support of the JOURNAL by the Division of Chemical Education which owns it.

It is perhaps not boasting too much to say that we have made the JOURNAL into the best organ in its particular field. To be sure, there are few competitors—a fact which may bear witness to our pre-eminence.

The number of our foreign subscribers and contributors is evidence of the respect in which we are held.

We have enlarged the conception of chemical education itself. I believe this is one of our most important successes. There is a fad for defining subjects in terms of activities; thus, "chemistry is what chemists *do*." In the same way it may be said: "Chemical education is what the JOURNAL OF CHEMICAL EDUCATION publishes." If this is true the field is indeed a large one—as it should be. Our responsibility as an educational periodical has not been only to teachers and their students; we have at least tried to serve the needs of chemists at all stages within the profession, as well as of lay readers outside it.

Many issues have arisen and disappeared in 15 years; we have participated in many of them; some of them are perpetual issues. We have fought and won a bitter war during this time, and argued about students and the draft, universal military training, deferment of chemists, shortage of scientific manpower, wartime production, and technical education. A hundred and eighty editorials have somehow found their way out of the editorial pen and onto this page—what a lot of words. A few of them have apparently been read, for they brought a response.

And now, after this issue, I pass on the editorial shears and wastebasket to my successor, William F. Kieffer, who has served for several years as an Associate Editor. The frontispiece is prophetic; it shows a younger man undertaking responsibility with enthusiasm. I am confident that he will maintain such traditions as deserve maintaining and make such changes as need to be made.

ONE last word before leaving the stage. Nothing gives me more pleasure than to call attention to the superlatively fine article by Dorothy W. Gifford on page 490. Any comment of mine is unnecessary and would probably be an understatement. Miss Gifford is not only an old friend of mine, but one of the most successful and enthusiastic secondary-school teachers I know, and I feel it is worth 15 years of waiting to publish her thoughts on the "Trends in high-school chemistry." I wish someone had established a prize for the best article published during the year in THIS JOURNAL. It would be hard to find a more appropriate recipient for such a prize.

STUDENT EXPERIMENTS INVOLVING SOME SOLID-GAS REACTIONS

E. A. PERETTI

University of Notre Dame, Notre Dame, Indiana

VERY few of the laboratory textbooks of physical chemistry have adequate experiments dealing with heterogeneous reactions of the gas-solid type, although they are of great industrial importance. In many processes simple decomposition reactions of the type Solid I \rightarrow Solid II + Gas are encountered, such as the decomposition of sulfides, carbonates, sulfates, and hydrates, to name only a few. Some of these reactions are not suitable for student experiments because of operational difficulties, but others can be the profitable subject of a two-period experiment. For metallurgy students we have developed two experiments in which cupric sulfide, pyrite, and copper sulfate are employed, but they can be used without major modification on other substances. One experiment leads to a knowledge of the phases involved and a measurement of the equilibrium temperature at various pressures; and the other gives the student an appreciation of the reaction rate.

In the first one the equilibrium temperature is determined by heating curves made at fixed pressures, and

hence, it is necessary that the reaction rate be relatively great and the heating rate low; otherwise high values are obtained.

Figure 1 is a photograph of the experimental setup, and Figure 2 is a schematic representation of the apparatus involved. In a Pyrex, Vycor, or quartz tube *C*, depending upon the temperature range, is placed a glass or quartz tube containing the powdered sample to be heated. A calibrated thermocouple *A* is imbedded centrally in the powder and is connected to oppose a second thermocouple, to allow measurement of the temperature of the sample and the difference in temperature between the sample and the outside of the reaction tube *C*. Thermocouple *A* is connected through an ice-water cold junction to potentiometer *N*, from whose e. m. f. can be obtained the sample temperature. The differential couple is connected to a second potentiometer *O*. The two thermocouples do not interfere with each other if both circuits are not closed simultaneously. If a double-pole, double-throw switch is

used for the thermocouple circuits, only one potentiometer is required. The reaction tube *C* is made to protrude from six to eight inches beyond each furnace end, keeping cool enough to allow connections to be made with rubber stoppers. Tube *C* is connected to a nitrogen tank *M* and a cold trap *D*. This in turn leads to a reservoir *I* and to two manometers, a closed-end type *E* and an open-end type *F*. To control the pressure inside the reaction chamber a manostat *G* is employed, such as the Greiner Cartesian model shown in Figure 1. Two needle valves *H* join the system to a vacuum pump *L*, and to the atmosphere. A tube furnace of the split type is admirably suited to this experiment.

In a typical run ten grams of powder is placed in the

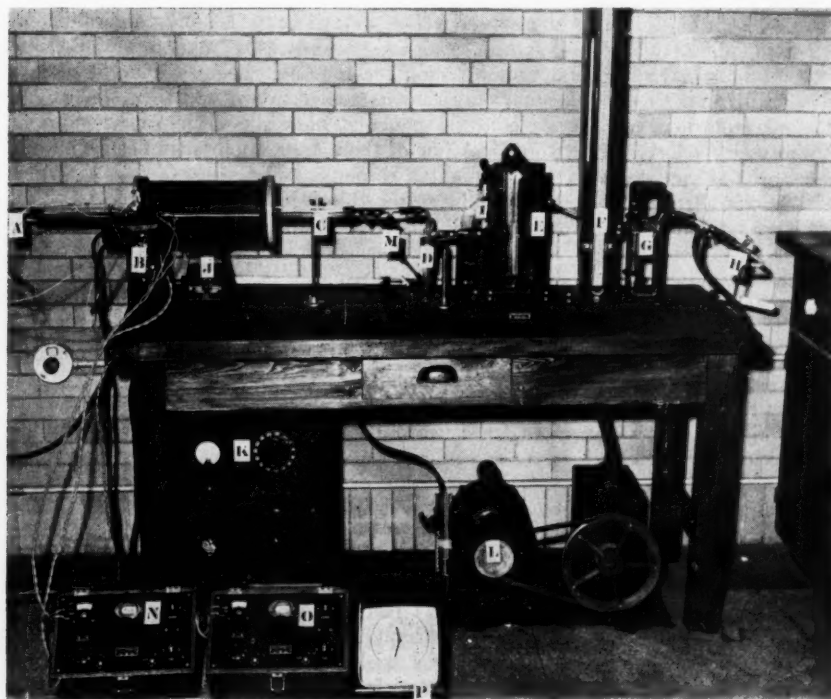


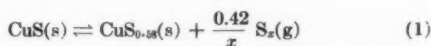
Figure 1.

reaction tube; all connections are made gas-tight, and the system is slowly evacuated to remove oxygen. The outlet to the pump is then closed and dried nitrogen is admitted. Evacuation and flushing with nitrogen are repeated several times, after which the pressure is set at the desired value. The furnace is then turned on, and potentiometer readings are recorded at half-minute intervals. A plot of e. m. f. versus time gives a heating curve from which the equilibrium temperature for each run is determined.

Samples are taken of the powder before and after each experiment. These are X-rayed and compared with standard patterns for phase identification.

Pyrite (FeS₂) and artificial CuS are both quite suitable for this experiment. Sulfur vapor from the decomposition of the solid condenses in the colder portions of the reaction tube before the equilibrium temperature is attained and assures the maintenance of a total sulfur pressure at the preset value. Figure 3 shows a plot of the logarithm of the total sulfur pressure versus reciprocal absolute temperature for CuS and FeS₂ as measured by students using the method herein outlined, and by Allen and Lombard¹ by a static method.

Instructive calculations can be made with the data as illustrated by the CuS, whose product of decomposition in this range of temperature and pressure is a phase whose crystal structure has been shown by Buerger² to be that of digenite, Cu₉S₅. The composition varies with temperature, but can be considered to be practically constant at CuS_{0.55} for the range of temperature of practical interest. The decomposition can be written:



As Kelley³ has shown, the sulfur vapor consists almost entirely of S₂, S₈, and S₈ molecules, so that:

$$P_{\text{total}} = P_{\text{S}_2} + P_{\text{S}_8} + P_{\text{S}_8} \quad (2)$$

and at equilibrium:



and:



whence:

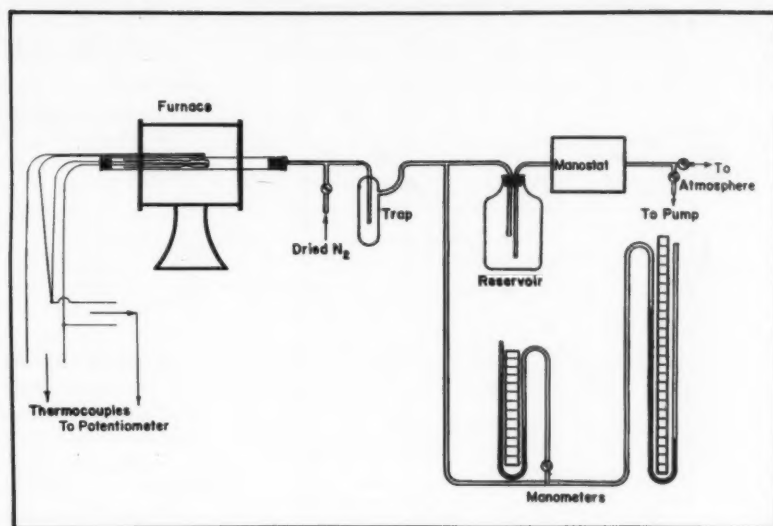


Figure 2.

$$K_3 = P_{\text{S}_2}^4 / P_{\text{S}_8} \quad (5)$$

$$K_4 = P_{\text{S}_2}^3 / P_{\text{S}_8} \quad (6)$$

and:

$$P_{\text{total}} = \frac{P_{\text{S}_2}^4}{K_3} + \frac{P_{\text{S}_2}^3}{K_4} + P_{\text{S}_2} \quad (7)$$

By substituting the free-energy equation for reactions (3) and (4) in $\ln K = -\Delta F^\circ / RT$, we obtain:

$$\log K_3 = \frac{-95,200 + 13.8 T \log T + 68.28 T}{4.575 T} \quad (8)$$

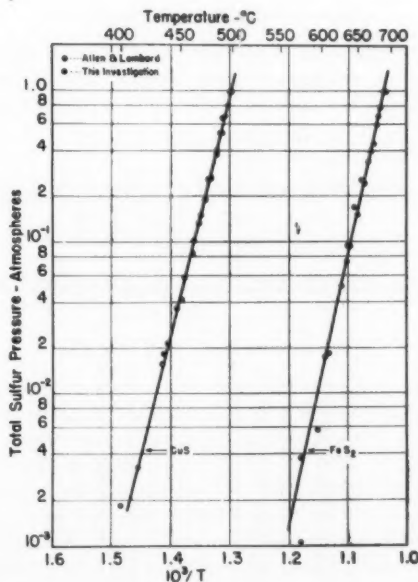


Figure 3. Logarithm of Total Sulfur Pressure Versus 1/T

¹ ALLEN, E. T., and R. H. LOMBARD, *Am. J. Sci.*, **43**, 175 (1917); *Econ. Geol.*, **32**, 253 (1937).

² BUERGER, N. W., *Econ. Geol.*, **36**, 19 (1941).

³ KELLEY, K. K., Bureau of Mines Bulletin No. 406, 2 (1937).

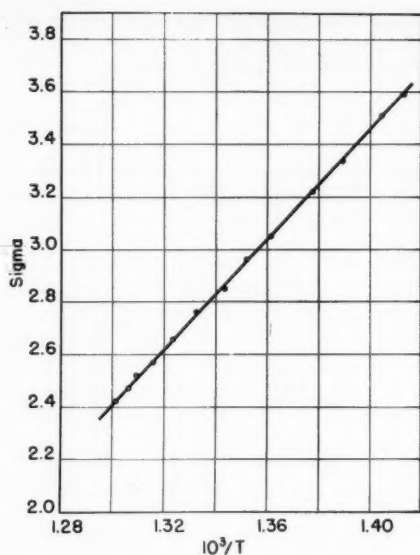
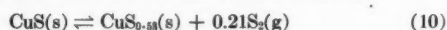


Figure 4. Sigma Function Versus $1/T$ for $\text{CuS}(s) \rightleftharpoons \text{CuS}_{0.55}(s) + 0.21\text{S}_2(g)$

$$\log K_1 = \frac{-64,088 + 9.2 T \log T + 44.26 T}{4.575 T} \quad (9)$$

Substitution of experimentally determined temperatures and pressures in equations (8) and (9) and (7) permits the calculation of the S_2 pressure values and hence the percentage of each molecular species in the gas.

In addition the student can make other approximate calculations. The reaction can be written:



The specific heat of the new solid phase is unknown, but can be estimated from Kopp's law to be 9.33. Using Kelley's values for CuS and $\text{S}_2(g)$ we obtain:

$$C_p: 0.21\text{S}_2 = 1.638 + 0.1865 \times 10^{-3}T$$

$$C_p: \text{CuS}_{0.55} = 9.330$$

$$\Sigma C_p: \text{Products} = 10.968 + 0.1865 \times 10^{-3}T$$

$$C_p: \text{CuS} = 10.6 + 2.64 \times 10^{-3}T$$

$$\Delta C_p = 0.368 - 2.4535 \times 10^{-3}T$$

where:

$$\Delta H = \Delta H_0 + 0.368T - 1.227 \times 10^{-3}T^2 \quad (11)$$

and:

$$\Delta F^\circ = \Delta H_0 - 0.848 T \log T + 1.227 \times 10^{-3}T^2 + IT = -RT \ln K_{10} \quad (12)$$

where:

$$K_{10} = (P_{\text{S}_2})^{0.21}$$

and:

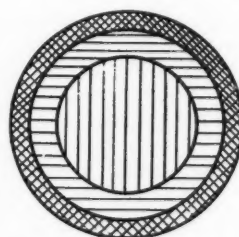
$$\text{Sigma} = \frac{\Delta H_0}{T} + I = -R \ln (P_{\text{S}_2})^{0.21} + 0.848 \log T - 1.277 \times 10^{-3}T \quad (13)$$

The sigma function is obtained by solving equation (13) for each experimental pressure and temperature as shown in the table. A plot of sigma versus $1/T$ (Figure 4) then yields a ΔH_0 value of 10,500, from which the integration constant I can be evaluated for each temperature (see the table).

The excellent agreement of the values for the integration constant is an indication of the self-consistency of the data; the average value for I is -11.24 . Substitution of the values for I and ΔH_0 in equations (11) and (12) then gives:

$$\begin{aligned} \Delta H_T &= 10,500 + 0.368T - 1.227 \times 10^{-3}T^2 \\ \Delta F^\circ &= 10,500 - 0.848 T \log T + 1.227 \times 10^{-3}T^2 - 11.24T \end{aligned}$$

The student is also in a position to estimate the heat



- CuO
- ▨—CuSO₄ · CuO
- ⊗—CuSO₄

Figure 5. Interfaces and Phases During the Decomposition of CuSO_4

and free-energy change of formation of the high temperature phase.

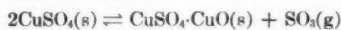
This procedure also gives excellent results with the

$T^\circ\text{K}$	Pressure, S_2		$-R \ln (P_{\text{S}_2})^{0.21}$	$0.848 \log T$	$-1.277 \times 10^{-3}T$	Sigma	$\frac{10,500}{T}$		
	atmospheres							I	
707.65	6.84×10^{-3}	2.08	2.42	2.42	-0.91	3.59	14.84	-11.25	
711.83	8.21×10^{-3}	2.00	2.42	2.42	-0.91	3.51	14.75	-11.24	
719.65	1.198×10^{-2}	1.85	2.43	2.43	-0.92	3.36	14.59	-11.23	
726.01	1.63×10^{-2}	1.72	2.43	2.43	-0.93	3.22	14.46	-11.24	
734.55	2.38×10^{-2}	1.56	2.43	2.43	-0.94	3.05	14.29	-11.24	
739.65	2.91×10^{-2}	1.48	2.43	2.43	-0.95	2.96	14.20	-11.24	
744.37	3.64×10^{-2}	1.38	2.43	2.43	-0.96	2.85	14.11	-11.26	
750.55	4.59×10^{-2}	1.29	2.44	2.44	-0.97	2.76	13.99	-11.23	
755.46	5.73×10^{-2}	1.19	2.44	2.44	-0.97	2.66	13.90	-11.24	
760.02	6.98×10^{-2}	1.11	2.44	2.44	-0.98	2.57	13.82	-11.25	
763.65	8.16×10^{-2}	1.05	2.45	2.45	-0.98	2.52	13.75	-11.23	
765.65	8.95×10^{-2}	1.01	2.45	2.45	-0.99	2.47	13.71	-11.24	
768.38	10.03×10^{-2}	0.96	2.45	2.45	-0.99	2.42	13.67	-11.25	
							Average =	-11.24	

decomposition of NH_4Cl , bringing out clearly the alpha-beta transition.

(11)

In a second experiment instructive rate studies of a solid-gas reaction involving a simple decomposition can be made by using anhydrous copper sulfate powder. Thirty-two grams of the CuSO_4 is briquetted at 3500 p. s. i. in a cylindrical mold having a cross-sectional area of one square inch, so that the height of the resultant briquette is greater than its diameter. Three or four of these are put into a preheated muffle furnace and quickly brought to temperature. At regular time intervals a briquette is removed from the furnace, quenched under a beaker with dry ice, and then cut in half transversally. This exposes the interior and clearly shows visually the progress of the reaction because of the different-colored products of the decomposition. A clear line of demarcation exists between the CuSO_4 (white to bluish white), $\text{CuSO}_4 \cdot \text{CuO}$ (yellow-brown) and CuO (black) (see Figure 5). The rate of advance of each interface can be measured readily, and hence the rate of the decomposition is obtained without time-consuming chemical analyses. Figure 6 shows the result of such an experiment at 850°C ., in which the progress of the reactions:



and:

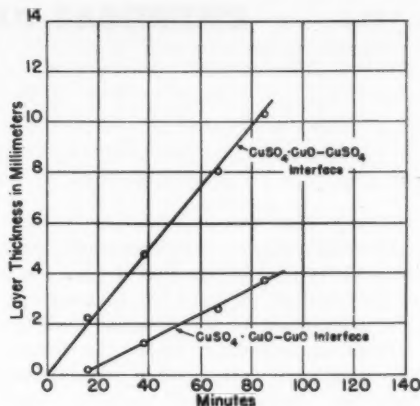
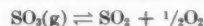
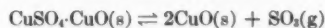


Figure 6. Thickness of CuO and CuO-CuSO_4 Layers at 850°C . as a Function of Time



have been followed simultaneously using four briquettes.

By pooling the work of several squads, each run at a different temperature, it is possible to obtain the activation energy for the solid-gas reactions.

EFFECT OF WATER ON THE INTERACTION OF ALUMINUM AND IODINE

SYED AZMATHULLHA and ARCOT VISWANATHAN
The New College, Madras, India

A DROP of water, or water vapor from salt hydrates, can initiate the combination of aluminum with iodine, as shown by the following experiment.

Thoroughly dry two grams of fine aluminum dust at 100°C . In a mortar which is completely dry mix the aluminum with three grams of sublimed iodine. Divide the mixture into four piles of equal size on a sheet of dry asbestos. On the top of each pile place one of the following: (a) one gram of thoroughly dry, anhydrous CuSO_4 ; (b) one gram of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; (c) one gram of

any hydrated alum; (d) (with care) a few drops of water. In all but the first case a dense violet smoke issues, sometimes after a few moments, and the metal ignites with a flash.

The ingredients should be used immediately after drying; otherwise they absorb traces of moisture which will cause reaction. Also, exercise great care in mixing the ingredients; be sure that they and the mortar are absolutely dry, or else there is danger of a sudden ignition, badly burning the hand.

CHEMICAL CARCINOGENS

JOHN R. SAMPEY

Furman University, Greenville, South Carolina

It is a sad commentary on the emotional and intellectual immaturity of America that it took the present storm on the relation of smoking to lung cancer to awaken the population to the dangers of carcinogens. Scores of emotion-packed articles on the theme, "cancer by the carton" have appeared in popular magazines throughout the country. And on the other side, through the daily press, radio, and television, the multimillion-dollar advertising interests of the tobacco companies have rushed to the defense of the industry.

One wonders how much understanding the general public has of how the final issue will be reached. The final decision will be made with little attention to the hue and cry now being raised. It will come after a long campaign in many scientific laboratories, and the results will be announced in the technical language of the medical literature. Already some 45 of these studies may be found in the current medical journals.

Chemical Carcinogens in Current Medical Literature

Chemical	No. of articles	Chemical	No. of articles
Acetylaminofluorene	48	Fats	9
Amino acids	6	Radioiodine	21
Aminoazotoluene	6	3'-Methyl-dimethyl-aminoazobenzene	17
Azo dyes	11	Methylcholanthrene	112
Benzenanthracene	8	Naphthylamine, beta	15
Benzidine	7	Nitrogen mustards	12
Benzpyrene	38	Petroleum	20
Beryllium compounds	6	Pituitary hormones	10
Carbon tetrachloride	6	Progesterone	5
Cholesterol	5	Silicates	5
Chromates	15	Stilbestrol	7
Cortisone	12	Tannic acid	8
Croton oil	22	Tars	6
Dibenzanthracene	25	Testosterone	8
Dibenzcarbazole	5	Thiouracil	11
Diethylstilbestrol	27	Tobacco	45
Dimethylaminoazobenzene	51	Trypan blue	7
Dimethylbenzanthracene	39	Urethan	25
Estradiol	16	Vitamins	7

Carcinogenesis became an experimental science 40 years ago when Yamagiwa and Ichikawa induced the first cancer by prolonged application of a coal-tar distillate to the ear skin of rabbits. For many decades the high incidence of skin cancer among the chimney sweeps of England had been considered an occupational disease. The discovery made by the two Japanese scientists opened the way for an experimental approach to the hazards of carcinogens in industrial operations.

The search today for carcinogenic agents has extended far beyond the bounds of industrial medicine.

The extent of the field may be visualized by summarizing some 850 articles of the last six years which describe experiments on the incidence of growth-promoting activity of numerous agents toward neoplasms (see the table).¹ Review articles and references to theoretical speculations and interpretations of mechanisms are not included in the 850 total.

Hydrocarbons account for one-fourth of all current studies on carcinogens, methylcholanthrene alone being the agent in more than 100 articles. Benzenanthracene, benzpyrene, dibenzanthracene, dimethylbenzanthracene, and petroleum are other hydrocarbons inducing a variety of neoplastic growths in animals.

Azo dyes and azo coloring materials used in foods have been tested extensively in the study of cancer of the liver. Dimethylaminoazobenzene (butter yellow), 3'-methyl-dimethylaminoazobenzene, aminoazotoluene, and other azo dyes have been employed to induce hepatomas in experimental animals.

The teacher of organic chemistry will note the relatively simple structure of other molecules in this list of powerful carcinogens: 2-acetylaminofluorene, amino acids, carbon tetrachloride, fats, beta-naphthylamine, nitrogen mustards, tannic acid, thiouracil, and urethan.

Inorganic chemicals are much more useful as anticancer agents,² but the cancer-inducing properties of beryllium compounds, chromates, radioactive iodine, and silicates have been investigated extensively.

The role of hormones in carcinogenesis is one of the most controversial subjects in the chemotherapy of cancer. Leading in the volume of current research are the sex hormones diethylstilbestrol, estradiol, progesterone, stilbestrol, and testosterone, the pituitary hormones, and cortisone.

One of the most intriguing problems of cancer arises from the strange dual role played by many chemical molecules which act as both carcinogenic and anticancer agents. A recent summary of the current medical literature shows that one-third of the most frequently employed anticancer agents are found among the present list of most used cancer-inducing chemicals. The chemicals appearing in both lists are: cortisone, nitrogen mustards, hydrocarbons, estrogens, amino acids, urethan, vitamins, pituitary hormones, and testosterone. If we include biological agents, then three more groups appear on both lists, namely: viruses, with 41 studies on their anticancer activity and 13 re-

¹ SAMPEY, J. R., *Am. J. Pharm.*, **127**, 53-64 (1955); *J. So. Car. Med. Assoc.*, In press.

² SAMPEY, J. R., *Ind. Med. and Surg.*, **22**, 300-1 (1953). *Studies*, **2** (No. 3), 12-18 (1955).

ports on their carcinogenicity; tumor extracts, which have called forth 18 studies on inhibiting cancer and 55 on inducing neoplasms; and extracts of normal tissues, which have rated 12 articles on anticancer studies and 18 on carcinogenicity.³

Currently the nation is spending some twenty-

million dollars annually on its cancer control program. In view of the little known about carcinogenic and anticancer agents and the daily death rate of 600 victims of this killer, we have much to do and much to learn. It is even conceivable that the present hysteria over cigarettes and cancer may result in more funds for basic research on the chemotherapy of neoplastic diseases.

³ SAMPEY, J. R., *Science*, In press.

CROSSWORD PUZZLE

BERT H. CLAMPITT
Oak Ridge, Tennessee

Across

1. Having pH less than 7
5. A measure of concentration (abbreviation)
8. Beige color
12. Cerium is a _____ earth
13. Exclamation
14. Son of Noah
15. Driving force of an electric current is the _____ force
18. TiO₂
19. Dismay
22. Er₂O₃
26. Suffix denoting fitness
27. Solid water
29. Earths
30. Large bird of Arabia
31. Compound having a $-\text{CH}_2-\text{O}-\text{CH}_2-$ linkage
32. Affirmative answer
33. Assert
35. Self
36. Wings
37. Cerium in +4 state
39. Conjecture
40. Positive ions
43. Temperature-measuring devices
49. Girl's name
50. Tease (variant)
51. Easy
52. Fish sauce
53. A beverage
54. Roentgen ray

Down

1. 100 square meters
2. Calorie (abbreviation)
3. Wrath
4. Ten-carbon hydrocarbon
5. Chlorobenzene is an ortho _____ director
6. Actinometers depend upon _____ reactions
7. Mother
8. Compounds formed by replacing the acid hydrogen by a hydrocarbon

1	2	3	4	X	5	6	7	X	8	9	10	11				
12	R	A	R	E	X	A	H	X	J	H	E	M				
15	E	L	E	C	T	R	O	M	T	I	V	E				
X	X	X	18	N	A	T	A	S	E	X	X	X				
19	D	A	U	N	T	X	O	X	22	E	R	B	T	A		
26	T	B	L	E	X	27	F	C	E	X	29	J	O	D	S	
30	R	O	C	X	31	E	T	H	E	R	X	32	Y	E	S	
33	A	V	E	R	X	35	S	E	L	X	36	L	A	E		
37	C	E	R	I	C	X	M	X	39	G	N	E	S	S		
X	X	X	40	C	A	T	I	O	N	S	X	X	X	X		
43	T	H	E	R	M	O	C	O	U	P	L	E	S	46	47	48
49	V	E	R	A	X	50	A	Z	X	51	E	A	T	H		
52	A	L	E	C	X	53	A	L	E	X	54	K	R	A	Y	

9. Greek letter
10. Speed up (as an engine)
11. Japanese apricot
16. An explosive
17. Suffix denoting a carbohydrate
19. Fermi _____ statistics
20. Over
21. An open sore
23. PV = constant; this law was discovered by _____
24. Notions
25. Donkeys
27. Pronoun
28. Lamprey
34. Form of openwork edging
36. An augur
38. A rotating projection
39. Antelope
41. Law of Moses
42. Soft mud
43. Tennessee Valley Authority (abbreviation)
44. Goddess of the dead
45. Before
46. Household god
47. Greek letter
48. Timid

(See page 477 for solution.)

FIVE-BLOCK MODIFIED LONG FORM PERIODIC TABLE
 With New Positions for Hydrogen and Helium

G. Ramirez Torres, University of Puerto Rico

The Primary Elements

Period	1s
1	1 ¹ H 1.008 2 ² He 4.003
2	
3	
4	
5	
6	
7	

The Alkali & Alkaline-earth Metals

The Representative or Regular Elements						
<i>p</i>						
The Primary Elements						
Period	1s	2s	3s	4s	5s	6s
2	1 ¹ H 1.008 2 ² He 4.003	3 ³ Li 6.940 4 ⁴ Be 9.012				
3	11 ¹¹ Na 22.997 12 ¹² Mg 24.31					
4	19 ¹⁹ K 39.098 20 ²⁰ Ca 40.08					
5	37 ³⁷ Rb 85.46 38 ³⁸ Sr 87.62					
6	55 ⁵⁵ Cs 132.91 56 ⁵⁶ Ba 137.34					
7	87 ⁸⁷ Fr 223.018 88 ⁸⁸ Ra 226.0254					

The Transitional or Related Metals

The Transitional or Related Metals										
<i>d</i>										
Period	1s	2s	3s	4s	5s	6s	7s	8s	9s	10s
4	21 ²¹ Sc 44.96 22 ²² Ti 47.88 23 ²³ V 50.94 24 ²⁴ Cr 52.00 25 ²⁵ Mn 54.94 26 ²⁶ Fe 55.85 27 ²⁷ Co 58.93 28 ²⁸ Ni 58.69 29 ²⁹ Cu 63.55 30 ³⁰ Zn 65.38									
5	39 ³⁹ Y 88.91 40 ⁴⁰ Zr 91.22 41 ⁴¹ Nb 92.91 42 ⁴² Mo 95.94 43 ⁴³ Tc 98.91 44 ⁴⁴ Ru 101.07 45 ⁴⁵ Rh 101.07 46 ⁴⁶ Pd 106.36 47 ⁴⁷ Ag 107.87 48 ⁴⁸ Cd 112.41									
6	71 ⁷¹ Lu 174.97 72 ⁷² Hf 178.49 73 ⁷³ Ta 180.95 74 ⁷⁴ W 183.85 75 ⁷⁵ Re 186.21 76 ⁷⁶ Os 190.23 77 ⁷⁷ Ir 192.22 78 ⁷⁸ Pt 195.08 79 ⁷⁹ Au 196.97 80 ⁸⁰ Hg 200.59									

The Lanthanum and the Actinium Series of Elements

The Lanthanum and the Actinium Series of Elements																	
<i>f</i>																	
Period	1s	2s	3s	4s	5s	6s	7s	8s	9s	10s	11s	12s	13s	14s	15s	16s	
7	57 ⁵⁷ La 138.91 58 ⁵⁸ Ce 140.12 59 ⁵⁹ Pr 140.91 60 ⁶⁰ Nd 144.24 61 ⁶¹ Pm (144) 62 ⁶² Sm 150.36 63 ⁶³ Eu 151.96 64 ⁶⁴ Gd 157.25 65 ⁶⁵ Tb 158.93 66 ⁶⁶ Dy 162.50 67 ⁶⁷ Ho 164.93 68 ⁶⁸ Er 167.26 69 ⁶⁹ Tm 168.93 70 ⁷⁰ Yb 173.05																
8	89 ⁸⁹ Ac 227.03 90 ⁹⁰ Th 232.038 91 ⁹¹ Pa 231.04 92 ⁹² U 238.03 93 ⁹³ Np 237.05 94 ⁹⁴ Pu 244.06 95 ⁹⁵ Am 243.06 96 ⁹⁶ Cm 247.07 97 ⁹⁷ Bk 247.07 98 ⁹⁸ Cf 251.08 99 ⁹⁹ Mt 258.11 100 ¹⁰⁰ Lr 260.10																

- Block Differentiating Electrons**
- I - s-type in the innermost or K-shell
 - II - (s)d-type in the outermost shell
 - III - p-type in the outermost shell
 - IV - d-type in the next-to-its-outermost shell
 - V - f-type in the second from the outermost shell

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STABILITY OF THE $1s$ ORBITAL AND THE CHEMICAL BEHAVIOR OF HYDROGEN¹

New Positions for Hydrogen and Helium in a Five-block Periodic Table

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HYDROGEN is considered to be one of the most unusual elements. It is described as an electropositive element which loses its electron readily, forming a positive ion which in solution becomes immediately solvated. Hydrogen and the alkali metals similarly have one valence electron in the s level. It is this one single s -type electron that is responsible for the same type spectrum emitted by these atoms, and for the formation of their simple, unipositive, gaseous ions. Because of these facts, hydrogen and the alkali metals are designated in standard spectroscopic notation by the same term symbol, and hydrogen is considered as an electropositive element similar to the alkali metals and is often made the lightest member of Group I in the periodic table. On the other hand, hydrogen is said to be predominantly non-metallic; it is strongly negative in character when in combination with strongly positive elements, where it appears as the negative hydride ion H^- ; it also forms covalent compounds with nearly all other nonmetals. For these reasons hydrogen is also considered as the lightest member of the halogen family. Because of this apparent ambiguity, hydrogen is given two opposite positions in many modern charts; simultaneously it is placed with the alkali metals and with the halogens.

We also find that many hydrogen compounds are considered to be partially ionic and partially covalent; in these compounds positive ionic character is given to the hydrogen. In many instances hydrogen appears to have properties other than those to be expected, and we are likely to dismiss the difficulty by concluding that hydrogen may be expected to misbehave because of its peculiar electronic structure.

I am of the opinion that there is no real ambiguity in the chemical behavior of hydrogen or in its natural position in the periodic table. The apparent ambiguity exists because of our misconception of the actual properties of hydrogen as an element.

As a matter of fact we all assume that the electronic structure of helium is the most stable one. It consists of a completed $1s$ orbital. The hydrogen atom, the simplest of all atoms, contains a single $1s$ electron and it should be natural to expect that hydrogen would assume its lowest energy state by completing its $1s$

orbital. The atoms of the alkali and the alkaline-earth metals contain, respectively, one and two s -type electrons in their highest energy level or outermost shell. They also have two completed subshells in the next to the outermost shell, except for lithium and beryllium which have only one.

A comparison of the chemical behavior of hydrogen and helium with that of the alkali and the alkaline-earth metals, all atoms of which are characterized by having s -type electrons in their outermost shell, will show that the $1s$ orbital is very different from all other s orbitals having a principal quantum number greater than one and in the highest energy level of an atom. In the case of the alkali and the alkaline-earth atoms these s orbitals will be designated as $(n > 1)s$ orbitals. It should also be pointed out that the difference between those two kinds of s electron is greater than the difference between the p electrons and the $(n > 1)s$ electrons.

The helium and the alkaline-earth atoms form similar doubly charged gaseous ions. Their spectra are very similar and their ground states are designated by the same spectroscopic symbol 1S_0 . But as said before, the helium atom is in the lowest possible energy state, while the barium atom is in a very high energy state. Thus, helium is chemically the most inert of the elements, while barium is among the most reactive. The $1s$ electrons in hydrogen and in helium are not readily transferable to other atoms, while the $(n > 1)s$ electrons of the alkali and the alkaline-earth metals are the most readily transferable.

The chemical differences between two atoms, one having a single electron in the $1s$ orbital and the other a single electron in an $(n > 1)s$ orbital, is even greater than between helium and the alkaline-earth metals. This is precisely the case of hydrogen and the alkali elements. While helium remains chemically indifferent, hydrogen, although not forming a positive ion, readily forms a negative ion as well as many covalent compounds. These are chemical properties not shown by the alkali metals. The $(n > 1)s$ electron in each alkali atom is even more readily available for electrovalence formation than the same type of electron in the alkaline-earth metals. The dissimilarity between the $1s$ and the $(n > 1)s$ orbitals having been established, it follows that hydrogen should no longer be considered

¹ Presented at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

chemically similar to the alkali metals merely because of its spectroscopic characteristic and designation.

Hydrogen, therefore, is a characteristic nonmetallic element, and it does not show any appreciable metallic properties or electropositive character as do the alkali metals. All of its chemical properties are perfectly accounted for in terms of the high stability of the $1s$ orbital, as compared with the high energy state of either the free proton or the ($n > 1$) s electrons in the outermost shell of the alkali and the alkaline-earth atoms. Hydrogen, accordingly, invariably reacts by completing the helium structure, either by pairing electrons to form covalent bonds, which may be polar or nonpolar, or by acquiring an extra electron to form the only simple hydrogen ion which is known to exist as a chemical entity, the negative hydride ion H^- .

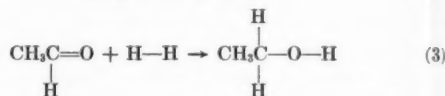
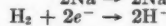
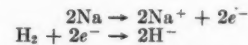
THE SIMPLE, GASEOUS, POSITIVE HYDROGEN ION OR FREE PROTON

The existence of the simple, gaseous, positive hydrogen ion, a free proton, has long been established. The proton is one of the fundamental particles in nature that enters into the composition of all nuclei, and therefore it cannot be considered as pertaining to or characterizing the hydrogen atom alone. It is produced in discharge tubes and in nuclear reactions. Under similar conditions, the gaseous positive ions of all the other elements can also be produced. The existence of a simple gaseous positive hydrogen ion cannot be taken as evidence that hydrogen is an electropositive element which loses its electron in a manner similar to the alkali metals. This evidence would be no more valid for the case of hydrogen than it would be for chlorine. Under the same conditions, chlorine forms a simple positive gaseous ion more readily than does hydrogen. With the exception of F, N, and O, it is easier to remove an electron from the atom of any other active element, or from Xe or Rn, than from a hydrogen atom. Even in the case of oxygen, recognized as one of the most electronegative elements, the energy difference between its ionization potential and that of hydrogen is less than 0.1 e.-v., as shown in the table. Not only does hydrogen hold its electron very firmly, but in addition it has a marked affinity for a second electron, as evidenced, first, by the great number of covalent compounds known in which hydrogen shares a pair of electrons with another atom, and second, by the existence of metallic hydrides

in which it has been shown definitely that the negative ionic component is the normal negative hydride ion. In fact, it seems that hydrogen most probably has never been freed of electrons in the course of ordinary chemical changes.

HYDROGEN AS AN OXIDIZING AGENT

There are many different kinds of reaction to which the term oxidation-reduction is applied. The term is used to designate reactions involving outright transfer of electrons as well as reactions in which there is a gain or loss in valence state, the so-called oxidation number, or where there merely occurs an exchange of bonds between different atoms. Illustrative examples are given below.



Hydrogen has always been considered to be a good reducing agent in terms of these oxidation-reduction concepts. But to consider hydrogen as a reducing agent in terms of the electron-transfer concept is inconsistent with the observed well known fact that no compounds of hydrogen are known in which this element is present as the positive ionic component, which would be the direct oxidation product of hydrogen. On the other hand, the direct reduction product of hydrogen, the normal negative hydride ion H^- , is known to exist. This seems to indicate that this element acts rather as an oxidizing agent than as a reducing agent in reactions involving outright transfer of electrons. Barium metal, for example, is vigorously oxidized to Ba^{++} by hydrogen (2) at $180^\circ C$. It should be pointed out that whenever reduction of the electron-transfer type takes place in the presence of hydrogen without the formation of the hydride ion, there is always present a third element, which in the final analysis turns out to be the net loser of the electrons. As for the hydrogen, it has appeared in the final products sharing its electron with another atom, and thus having been neither oxidized nor reduced.

In the reduction that takes place when hydrogen is passed over heated copper oxide, the reducing agent, presumably, is the very reactive oxide ion O^{--} , which on losing its extra electrons to the cupric ion, combines with hydrogen to form the more stable water molecule. Energetically, it would have been impossible for the electrons to have come from the hydrogen; on the contrary, it has been reported (2) that metallic copper reacts with hydrogen at $250-400^\circ$, to form a transient, volatile hydride. That the oxide ion may lose its two extra electrons to a metallic ion, even in the absence of hydrogen, can be observed when silver oxide or mer-

First Ionization Potential of Some Atoms (1)

Element		In kg.-cal./mole ($25^\circ C.$)	In electron-volts
He		568.34	24.65
Ne		498.34	21.63
A	F	403.25	17.49
		364.83	15.82
Kr	N	336.91	14.61
		324.25	14.05
O		315.45	13.68
	H	315.00	13.66
Xe	Cl	300.34	13.03
		281.14	12.19

(All other elements have lower values.)

curic oxide is heated to 300° or to 100°, respectively. Molecular oxygen and the free metals are obtained.

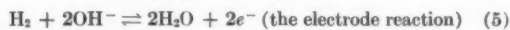
THE HYDRONIUM ION

It is generally recognized that hydrogen never takes part in chemical reactions as an independent proton. Nevertheless, it is common practice to write the formula for the "hydronium ion" as H^+ rather than H_3O^+ , on the assumption that it is more consistent to recognize the existence of solvation and then write all ions as unsolvated than to solvate the proton arbitrarily and leave all ions unsolvated.

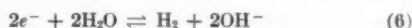
The consideration of the hydronium ion as a normally hydrated hydrogen ion or solvated proton, in a way similar to the normal hydration of other ions, is essentially the same thing as to say that the element hydrogen, like the alkali metals, easily loses its electron. Thus, hydrogen would be behaving chemically as a typical electropositive element, which is in direct contradiction to many of the experimental facts already mentioned. For example, the potassium ion is known to exist unhydrated as a chemical entity, while the simple positive hydrogen ion is not. If a potassium salt is dissolved in water, the potassium ion becomes normally hydrated. But there is no cationic hydrogen compound with which we could do the same thing and obtain something that similarly could be called a normally hydrated hydrogen ion. Theoretical calculations (3) of the hydration energy of the hypothetical simple positive hydrogen ion H^+ have led to the conclusion that it cannot exist in solution as an independent or normally hydrated ion. The anomalously high value obtained, from 260 to 277 kg.-cal./mole, several times greater than that for any other ion of corresponding radii, seems to indicate that this ion, unlike common ions, is definitely chemically hydrated. Of course, once the hydronium ion is formed independently of free protons, then, like any other ion, it may undergo normal hydration. It is this latter hydration that can be omitted in order to be consistent with the common practice of not indicating the normal hydration of all ions. Formaldehyde has the formula $C(H_2O)$, but it is not a hydrated carbon atom.

Although we may not know the exact formula for the hydronium ion, it has no relation at all to ionic hydrogen. As pointed out before, the only chemical form in which ionic hydrogen is known to exist is as negative H^- . The hydronium ion is a complex ion. It has its own properties and not the properties of any of the particular hydrogen atoms in the complex, and no one of these hydrogen atoms has an empty s orbital which could serve to differentiate it from the other hydrogen atoms. If this were the case, the normally hydrated proton would be a much stronger oxidizing agent than fluorine. The symbol H^+ should be reserved exclusively for the proton and for the hydrogen nucleus, and the formula H_3O^+ should be retained for the hydronium ion, as the formula for liquid water is written in the monomeric form, H_2O , although its actual structure is more complicated.

It seems that the most stable form of hydrogen is that associated with the completed $1s$ orbital. Since in the negative hydride ion the number of electrons held by the unipositive nucleus has been increased 100 per cent over the number previously held in the neutral atom, this ion should not be very stable as compared with the fluoride ion, in which the electron increase is only 11 per cent for a nucleus with nine positive charges. Therefore, first, we should expect hydrogen to form mainly covalent compounds in which its $1s$ orbital is completed by electron-pair sharing; and second, in the case of hydrogen compounds in which a molecule may split or dissociate into two or more molecular species or ions, we should expect that the hydrogen atoms in these dissociation products would maintain their respective $1s$ orbitals complete. When there are not enough electrons the bond will break, dividing the electron pair between the hydrogen and the other atom. We shall see that the hydronium ion behaves in this manner. Energetically, it is very unlikely that the hydronium ion is formed by the direct interaction of hydrogen gas and molecular water, as is usually indicated in the hydrogen electrode half-reaction: $H_2 + 2H_2O \rightleftharpoons 2H_3O^+ + 2e^-$. Instead, I believe that the hydronium ion, in nearly all cases, comes from the ionization of the water. Water complexes like dihydrol, for example, will ionize according to the complete- $1s$ -orbital principle stated above, into hydronium and hydroxyl ions. Now the hydrogen gas, catalyzed by Pt, will react with the very active OH^- ion to form water, and its extra electron is discharged at the electrode. As the OH^- ions are consumed and electrons are removed, more water ionizes to restore the displaced equilibrium, with the result that equivalent amounts of hydronium ions are released and accumulated. The equilibrium reactions involved are the following:



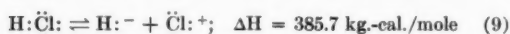
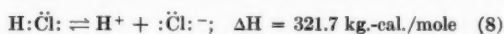
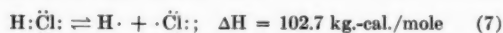
The proposed mechanism, equation (5), for the hydrogen electrode half-reaction is supported by the work of Delahay (4) and Eyring, Glasstone, and Laidler (5). These authors have demonstrated that during the electrolytic reduction of water it is molecular water and not hydronium ion which is reduced, as is indicated in equation (6).



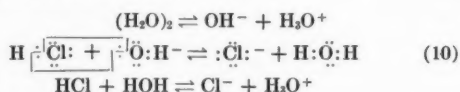
Except for the order in which they are written, equations (5) and (6) are identical.

In a similar manner we could account for the formation of the hydronium ion when an acid, such as HCl, is dissolved in water. Before writing the equations involved, it would be convenient to recall that when the complete- $1s$ -orbital principle for the hydrogen atom cannot be attained, the covalent bond, whether polar or nonpolar, will break, dividing the electron pair between the hydrogen and the other atom. This follows from energy considerations. In the case of the gaseous dissociation of the HCl molecule the energy of formation of

the H^+ and Cl^- ions from the atoms is 219 kg.-cal./mole, that of the ions H^- and Cl^+ is 283 kg.-cal./mole, and that of HCl is 102.7 kg.-cal./mole, values taken from Pauling (6). Evidently the first of the following reactions is the most likely to occur.



When HCl is dissolved in water it will react with the hydroxyl ion coming from the ionization of the water according to equation (10):



As chloride ions are formed equivalent amounts of hydronium are released. The OH^- loses its electron to the chlorine atom, and the neutral hydrogen atom from the HCl immediately forms a covalent bond with the unpaired electron of the neutral OH group, forming water. The neutral OH group has an electron affinity of about 50 kg.-cal./mole (7) which is much less than that of the chlorine atom, 85 kg.-cal./mole. The HCl molecule breaks, as shown under the lowest energy requirement process of equation (7).

NEW POSITIONS FOR HYDROGEN AND HELIUM IN A FIVE-BLOCK PERIODIC TABLE

We shall not recount the historical development of the periodic table. A review of the most important types of periodic chart that have been published up to 1934, including an extensive bibliography, is to be found in a series of papers by C. N. Quam and M. B. Quam (8). Moeller (9) gives a good, short account of the more significant developments up to 1948. Luder (10) and Simmons (11), present a brief chronological relation of the development of the modern forms of charts based on quantum numbers. Other modern proposals are listed under reference (12).

The facts and considerations presented in this paper have led the author to recognize that hydrogen and helium constitute a distinctive type of element different from the alkali and the alkaline-earth metals; that they should no longer be placed with the latter elements in Groups I and II of the periodic table; that hydrogen, notwithstanding the fact that it has many nonmetallic characteristics in common with the halogens, should not be classified together with these elements in the same periodic group, as hydrogen has a single $1s$ valence electron while the halogens have p valence electrons. Accordingly, it is hereby proposed that new positions be assigned to hydrogen and helium in the periodic table, in which they will constitute a section or separate block to be known as the $1s$ block or as "the primary elements."

It is also recognized that the alkali and the alkaline-

earth metals constitute another distinctive type of element with no relation at all to the rest of the representative or regular elements, that is, with Periodic Groups III, IV, V, VI, VII, and VIII. The elements of Groups III, IV, V, VI, and VII have p electrons in the outermost shell and they should be predominantly non-metallic. Many of these elements are amphoteric and show metallic properties, but these properties are not inherent to the p orbitals; they develop as a result of a decrease in the electron affinity of the atoms as the number of screening electrons and the atomic radii increase with increasing atomic numbers. On the other hand, the metallic properties shown by the alkali and the alkaline-earth metals are inherent in the ($n > 1$) s orbitals. To take care of this other situation it is also proposed that the eight classical groups of the representative elements be separated into two independent sections of the periodic table as suggested by Simmons (11): a two-group section constituted by Groups I and II headed by Li and Be, respectively, and the other, a six-group section composed of Groups III, IV, V, VI, VII, and VIII headed by B, C, N, O, F, and Ne, respectively. The former section is to be known as the ($n > 1$) s block or as "the alkaline and alkaline-earth metals." The latter section will be designated as the p block and will retain the name of "the representative or regular elements."

The scheme proposed above, together with a consideration of the tabular form of charts (13, 17) led us immediately to a five-block periodic table of the type based on electronic configuration of the atoms where the sublevels $1s$, ($n > 1$) s , p , d , and f are the distinguishing characteristic of each block, respectively. The chart obtained is similar in many respects to Simmons' (11) four-block table and Babor's (14) modification of Luder's (10) three-block periodic chart.

The Luder-Babor table is an elaboration of Ebel's (15) arrangement and of Gardner's (16) chart, and is based on atomic number and electron configuration. The chart is divided into three blocks: the sp block (the representative elements) with the differentiating electron in the highest energy level; the d block (the related or transitional metals) with the differentiating electron in the second highest energy level; and the f block (the lanthanum and actinium series of elements) with the differentiating electron in the third energy level.

Simmons' table is constructed from a modified Rydberg series by an entirely arithmetical process. It is called the "Arithmetical Table." This four-block table is similar to a reversed Luder-Babor chart with the alkali and the alkaline-earth metals placed in an additional separate block, which is the first block starting from the right-hand side of the chart. The block designation is as follows: The s block, to which no specific name is given, is headed by hydrogen and helium. To emphasize the chemical difference between them, these two elements are separated by a horizontal line from the remainder of their respective columns, the alkali and the alkaline-earth metals; the second or p

block corresponds to the representative elements and is headed by B, C, N, O, F, and Ne; the third or *d* block, the transitional elements, and the fourth or *f* block, the rare-earth elements.

A brief description of the modified periodic table is given below. The arrangement is fully illustrated. The elements are classified into as many sections or blocks of similar series as there are different types of energy sublevel, that is, into *1s*, ($n > 1$)*s*, *p*, *d*, *f*, *g*, *h*, . . . blocks, respectively. Since the number of elements known today is 100, at present there are no more blocks beyond the *f* block. Each series in a given block contains, when completed, a number of elements equal to the maximum number of electrons that can be accommodated in its distinguishing energy sublevel, *i. e.*, 2, 2, 6, 10, and 14, for the *1s*, ($n > 1$)*s*, *p*, *d*, and *f* sublevels, respectively. The elements in a particular series are differentiated from each other by the number of electrons in the distinguishing sublevel, except lanthanum.¹ Each block is divided into periodic groups or families of elements in number equal to the number of elements in a completed block series.

The first block, known as the *1s* block or the primary elements, is constituted by hydrogen and helium. The importance of these two elements is thus made conspicuous and for the first time they are given a definite position in the periodic system. It is a two-element block because only two elements can have *1s* electrons in the outermost shell of their atoms in their ground states. The second, or ($n > 1$)*s* block, is called the alkali and alkaline-earth metals. The third, or *p* block, known as the regular or representative elements, is constituted by the B, C, N, O, F, and Ne groups. The remaining blocks are: the fourth, or *d* block, the related or transitional metals, and the fifth, or *f* block, the lanthanum and actinium series of elements. In this chart the order of atomic numbers is not interrupted. All energy levels are sharply separated from each other and gaps are not greater than those imposed by the Bohr-Stoner atom-building-up principle. The number of electrons in the inner completed levels is indicated by

¹ The position of lanthanum is based on its chemical properties.

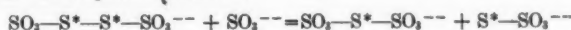
figures at the left of each block-series, and under each element its peculiar differentiating electronic configuration is given. Atomic numbers and atomic weights are also indicated. The electronic configurations were compiled from Carroll and Lehrman (17), except for the rare-earth elements and the transuranium elements, which were taken from Yost, Russell, and Garner (18) and from Seaborg (19), respectively.

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ERRATUM

IN THE paper, "Two experiments for the radiochemistry laboratory," in the June issue, the chemical equation which appears on page 331 is incorrect. The sulfur in sulfite ion should not bear an asterisk. This equation should be:



BUNSEN'S TRANSFER FROM CASSEL TO MARBURG

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FRIEDRICH STROMEYER, professor of chemistry at the University of Göttingen, died on August 18, 1835. Bunsen, then 24, and *Privatdozent* at Göttingen since 1834, was given the interim appointment. He offered a five-hour course in theoretical chemistry, accompanied by the necessary experiments, and a private course in stoichiometry. He also had to take over the direction of the laboratory. Friedrich Wöhler, who was then professor at the *Gewerbeschule* in nearby Cassel, was named permanent professor at Göttingen and assumed this important post at Easter in 1836. Bunsen's application for the vacancy at Cassel was supported by Wöhler and especially by Hausmann, whose courses in geology and mineralogy had been enthusiastically pursued at Göttingen by Bunsen. Hausmann wrote:

I have known Mr. Bunsen very well for many years and I can testify that he possesses excellent knowledge of the natural sciences, especially chemistry and physics, and further that with regard to character and behavior he has invariably conducted himself perfectly. In addition to his exceptional knowledge and the ability to transmit it, he also has much practical and mechanical talent.

Wöhler wrote that among the younger scholars known to him, Bunsen appeared to be the most suitable teacher of chemistry and chemical technology for the upper *Gewerbeschule*. "He has the additional special advantage of being a good mineralogist and of being competent in mathematics." There were three other applicants, including Dr. Carl Winkelblech, then assistant in the chemical laboratory at the University of Marburg. The records state that the latter "though possessed of good chemical knowledge, knew less of chemical technology, and nothing of geognosy and mathematics, and furthermore had less general training and unpretentiousness than Dr. Bunsen."

After some negotiations regarding salary—500 talers was proposed at first—the figure was finally fixed at 650 talers, which equalled his Göttingen income, and Bunsen was appointed teacher of chemistry and chemical technology at the upper *Gewerbeschule* in Cassel. The Elector signed the "highest rescript" on March 30, 1836, which was Bunsen's twenty-fifth birthday.

At Göttingen, Bunsen had carried out some minor researches on the preparation and analysis of several compounds of double cyanides with ammonia. His

chef d'oeuvre during this period was the important discovery that ferric hydroxide is an effective antidote for arsenic; even today freshly precipitated hydrous ferric oxide is used for this purpose. At Cassel he continued his work with arsenic and began his classic researches on cacodyl compounds. This was a poor choice in view of the facilities afforded by the school. The chemical laboratory on the second floor of the building consisted of a large storeroom and a smaller room, the actual laboratory. The latter was not really furnished for chemical work, since it lacked not only gas and water supplies, as was to be expected in those times, but there was no provision for ventilation.

Ordinary analytical studies could be conducted in such surroundings, but to attempt work with the self-flammable, noxious, evil-smelling, highly toxic cacodyl compounds was sure to lead to dangerous situations. On November 9, 1836, Bunsen lost most of the sight of his right eye, when attempting to determine the arsenic content of alkarsin (cacodyl oxide) by heating the sample with potassium chlorate or sodium nitrate. Probably the most toxic of the many derivatives he prepared and analyzed was cacodyl cyanide, and he hovered between life and death for several days because he was careless in handling this substance.

Although this series of researches lasted for five years, the greater part of the studies was carried on at Cassel. His constant appeals for improved facilities were turned down regularly with the statement that no money was available. Later Bunsen told his friend Debus:

One day when I knew that the Minister Freiherr von Hanstein was coming, I took a tube of cacodyl and laid it open in my laboratory and closed the windows and door. When he came I once more brought the conversation around to the poor ventilation and closed with the remark: "Excellency, would you care to see for yourself?" He crept in but jumped out at once. The next day an architect arrived and all was soon changed in accord with my wish.

The cacodyl researches had a permanent influence in the development of chemistry. They not only contributed much to the establishment of the radical theory, but they also led to Frankland's study of organometallic compounds, to the study by Frankland and Kolbe of the valence of elements, to Kekulé's recognition of the quadrivalence of carbon, and thus to the

modern structure theory. In Cassel, Bunsen also laid the foundations for his future work in analytical chemistry, and his investigations there of the processes occurring in the blast furnaces and furnaces used for smelting copper-bearing shales of the duchy led to his becoming interested in gas analysis, a field to which he contributed significantly. In fact, he was forced to devise apparatus and procedures, so that he may justly be called the founder of gas analysis in its broader sense. His suggestions regarding the use of the hitherto useless hot gases, which were simply allowed to escape into the air, led to a veritable revolution in the smelting industry, not only in Hesse, but later in England and other countries. It should also be remembered that he carried out his theoretical calculations regarding the useful employment of the heat values before the enunciation of the general energy law. He brilliantly chose the correct procedure. In view of these and other accomplishments, it was not surprising that the eyes of the outer world were turned on the gifted young teacher and scientist, and that the ducal authorities saw that his talents were rewarded and used in a school of higher rank than the *Ge-uerbeschule* in the capital city of Hesse.

Bunsen was a personable young bachelor and in demand at social gatherings. Despite determined efforts by eligible ladies, and perhaps the conspiring machinations of faculty wives, Bunsen remained unmarried all his life. When he came to Cassel, his cousin, also named Robert Bunsen, physician to the Elector, introduced him into a group of fun-loving young men whose lives were punctuated by humor and merriment. This group included Schwarzenberg, secretary to the Board of Mines, the two Arnoldi brothers, proprietors of a wallpaper factory, and the two Bunsens. One of the Arnoldis was a good man with pencil and brush, and there still exists a drawing showing the group as they probably would look 50 years later. The stoutish old men sit there, pipes in mouth, and Bunsen, a typical confirmed bachelor, smoking-cap on head, regards the others benevolently and strokes a lap dog. Arnoldi was doubtless also the creator of the two colored farcical sketches which were inspired by Bunsen's transfer from Cassel to Marburg in 1839.

TRANSFER TO MARBURG

The situation in the chemistry department at the University of Marburg had become acute. The incumbent since 1850 was Ferdinand Wurzer (1765-1844), who had studied in Paris during the time of Lavoisier. He had been there during the Reign of Terror and it was said that his hair had turned white because of his horror and grief over the execution of Lavoisier on May 8, 1794. However, despite the teachings received first hand from the great reformer of chemistry, Wurzer, originally a physician, still retained certain alchemical notions and as late as 1823 published a paper on the alleged formation of mercuric sublimate

during the preparation of hydrochloric acid from salt and sulfuric acid. He had to his credit the installation of a teaching laboratory at Marburg, and he conducted the practical work as long as his physical strength permitted. Carl Winkelblech (1810-65), who had been one of Bunsen's competitors for the post at Cassel, had the uncommon distinction of having become a *Privatdozent* at Marburg two weeks before attaining the doctorate on March 27, 1835. Because of his "excellent scientific accomplishments"—he had done some insignificant work on sulfur compounds and cobalt and lead oxides—he was promoted to associate professor in September, 1837. Actually, he had shown good teaching abilities, and the infirmities of Wurzer (now 72) made it imperative to provide the latter some relief. (There was no compulsory retiring age.) Finally, in January, 1839, Wurzer petitioned that he be relieved entirely of the direction of the teaching laboratory but be allowed to continue his lecture course in general chemistry and to carry on his other academic duties.

After some negotiations between the medical and philosophical faculties and the academic senate on one hand, and the Hessian ministry on the other, it was finally decreed (on August 7, 1839) at the highest level—i. e., by rescript of the Elector—that Dr. Bunsen in Cassel would be transferred to Marburg at an annual salary of 650 talers (one taler equals about 75 cents), and the incumbent associate professor Winkelblech would then proceed to Cassel in Bunsen's place.

This decision aroused much antagonism in Marburg. It was pointed out by the senate that a regulation of 1833 gave this academic body the right to be heard in matters concerning any new appointments, and therefore its feelings were all the more painfully wounded by this unexpected action. It stressed its opinion that Professor Winkelblech had rendered very satisfactory service and suggested that he be made director of the Chemical Institute. The pharmacy students sent a petition along the same lines to the prorector—i. e., the presiding officer of the senate. The latter also received a heated letter from Liebig, who had read of the matter in the newspaper. He expressed his "thunderstruck amazement concerning this unheard-of measure by which a university faculty member was offhandedly demoted to a trade school." Such a thing had never happened in Germany and would do the University of Marburg great harm; no one would accept a call to this university, where there was danger of being subjected to such highhanded treatment. Winkelblech was an excellent scientist and had developed the chemical department into one of the best in Germany. Liebig did not dare to discuss the matter with others lest an infinitely disgraceful light fall on the Hessian government. The ministry was sent a copy of this letter, but was not sufficiently impressed to alter its decision. The senate was instructed that it needed to be heard only in "suitable cases." The present in-



Figure 1

stance involved "higher and more general considerations, which were beyond the purview of the senate" and furthermore the matter at hand was not the calling of a professor but merely the transfer of two "civil servants."

Although the language was unwarrantedly ungracious, and cast an unfortunate aspersion on the understanding of the faculty members, subsequent events proved that the ministerial decree was a wise one. Who today knows anything of Winkelblech? He accepted the post at Cassel and contributed nothing of scientific value thereafter. After being accused of plotting against the state in 1853, he served a jail sentence of three months. In 1860 he was committed to a mental institution in Baden, and after prolonged treatment was able to resume part of his duties at Cassel. He died of a stroke on January 9, 1865. He is a typical example of a nonentity who escaped

oblivion only through accidental association with the career of an immortal.

Although the decision of the ministry turned out extremely well and was possibly dictated by its appreciation of Bunsen's superior promise as a scientist and teacher, actually the deciding factor was the fact that Winkelblech and Wurzer were incompatible, and the younger man had to go. On October 21, 1839, Bunsen was formally installed in the presence of the prorector and the dean of the medical faculty and, after the unbroken seals were removed from the doors and cupboards, the laboratory was turned over to him as supervisor *in loco* Professor Wurzer. It was part of his duty to provide the latter with the auditorium for his lectures and also to place at his disposal the necessary chemicals and a competent attendant. However, the administration was not willing to give the young associate professor unlimited authority and a quarterly inspection was ordained by Gerling, the professor of mathematics and physics. This custom was kept in force until Bunsen was promoted to full professorship in July, 1841, with the annual salary of 800 talers. He was then made titular head of the chemical laboratory, a step which undoubtedly was hastened by an inquiry from the University of Dorpat as to whether he would consider a call to that school.

Bunsen's departure from Cassel was regretted by his friends and gave rise to the two humorous caricatures reproduced here. The originals were and presumably are still in the archives of the University of Marburg.¹ They testify to the esteem in which young Bunsen was held.

The first cartoon (Figure 1) bears the caption: "Chemistry departs from Cassel. The Nature Society, its president at the head, gives it escort. Groans and tears form the foreground." While the watchman waves the banner from the belfry of the old St. Martin church, and the great statue of Hercules in the background is also decked with flags, the many-breasted figure of the sciences stands in the foreground, surrounded by the members of the Society, ceremoniously attired in top hats and bearing immense crying cloths. The banner of the Society is draped with mourning. Streams of tears course down the handkerchiefs, which are large as bed sheets, and collect to form a lake of tears in which a small dog is threatened with drowning. The long and lanky form of the departing Bunsen is shown with a knapsack over his back and an umbrella in his hand. His handkerchief droops far out of his back pocket. Headed in the direction indicated by the signpost "To Marburg," he passes by the Tree of Knowledge, up whose trunk the serpent winds toward the luscious ripe fruits.

The second cartoon (Figure 2) has the caption: "How chemistry is introduced into Marburg." It

¹ A technician who was engaged in photographing certain documents in the archives gave photographs of these Bunsen prints to Dr. Fritz H. Dersch, now of Binghamton, N. Y. He in turn provided one of the authors with copies. This kindness is gratefully acknowledged. To our knowledge, the prints have not been published before.

pictures Bunsen, his beloved pipe in mouth, diligently reading a book, and perched on a wheelbarrow. The latter is laden with retorts and other chemical equipment. The motive power is provided by a Hessian peasant wearing a heavy fur cap on his long hair. In the background is a simplified outline of St. Elizabeth's church in Marburg and in the far distance are the ruins of the Frauenberg.

TEACHING AND RESEARCH AT MARBURG

Bunsen remained at Marburg 12 years. During this period he developed a well-rounded chemical curriculum and persuaded the authorities to give him more space. The original laboratory budget of 600 talers was eventually increased to 1000 talers. Bunsen was an effective lecturer and spent much time in the laboratory with the students, even the beginners. He devised numerous simple but impressive lecture-demonstration experiments, and some of these were published by his hearers. Some of the best never were put into print. Besides general and inorganic lectures, he gave a one-hour course on Saturdays, from twelve to one, on stoichiometry, open to the public. In summers, from seven to eight, he lectured on organic chemistry, employing in general the dualistic and radical system of Berzelius. The public lecture course in summer dealt with electrochemistry, and always drew capacity audiences.

Bunsen's method in the laboratory was usually to demonstrate the experiments to the students, who then were expected to repeat them. The introductory exercises with the blowpipe, for instance, were followed by simple qualitative analyses requiring the simplest reactions, and then mixtures were given for analysis. The advanced students were quickly taught to rely on themselves when possible. Bunsen warned them against blindly accepting what was printed in the literature, recommending their own observations instead. He was even known to tell them not to read.

Despite the grief these dangerous substances had caused him Bunsen continued his work on cacodyl compounds. He left this field in 1841, when he had reached a satisfactory stopping place, from then on limiting his researches to inorganic and physical topics. In accord with his great interest in mineralogy and geology he devoted much time to the analysis of rocks and waters. These often taxed his analytical skills to the limit; he accepted such challenges and frequently devised new analytical procedures to fit the case at hand. One of the great triumphs of his Marburg period was the invention of the Bunsen cell, *i. e.*, the carbon-zinc element immersed in a mush of sand and concentrated nitric acid. The latter was later replaced by chromic acid. The grease-spot photometer also was devised during this period.

Bunsen's vacations were usually devoted to foreign travel: England, France, Italy, Sweden. Business was combined with pleasure and he returned home laden with new ideas and samples to be analyzed. His most famous journey, that to Iceland in 1846, led to

new theories regarding geyser action and formation of rocks.² It took him no less than six years to work up the mass of samples yielded by this scientific expedition. In contrast to the procedures he had learned from the excellent analyst Stromeyer,³ Bunsen used much smaller test portions and was able to finish a complete silicate analysis in from eight to ten days, instead of several months. Is it any wonder that he once said: "Whoever can do a perfect silicate analysis can do anything in analytical chemistry"? He devised marked improvements in the Liebig procedure for the determination of carbon and hydrogen by combustion but never published these advances. It remained for

² For an extended account, as given in letters to his mother, see FREUDENBERG, K., AND R. E. OESPER, *J. CHEM. EDUC.*, **18**, 253 (1941).

³ Regarding Stromeyer and his educational methods, see LOCKEMANN, G., *J. CHEM. EDUC.*, **30**, 202 (1953).



Figure 2

one of his students, Hermann Kolbe (1818–84), to make them known to the chemical world in the famed "Handwörterbuch der Chemie," of which he was the editor.

BRESLAU AND HEIDELBERG

Bunsen's reputation steadily rose to the point where it was inevitable that other schools would seek to lure him from Marburg. The University of Halle called him, but he refused because his laboratory budget had recently been increased to 1000 talers and his salary to 1200 talers (about 900 dollars). However, this same year (1850) he accepted a call to Breslau largely because he was promised a new building, to be erected according to his own plans. A short while later Heidelberg offered him the distinguished chair of Leopold Gmelin (1788–1853), but he felt bound to keep his promise to the Prussian authorities. His decision to leave Marburg was in large part the result of the worsened political conditions; an autocratic, reactionary regime had come into power and the democratic Bunsen could not abide this atmosphere. His suggestion that Kolbe be named his successor was followed.

Bunsen arrived at Breslau in April, 1851. The laboratory, housed in a former monastery, was in terrible condition. He wrote to one of his friends in Marburg: "It is now the morning and the evening of the seventh day and I am still not finished cleaning out this Augean stable." He missed his Marburg friends and also the beautiful hills and valleys. The faculty was cordial but he became intimate with only one, Gustav Kirchhoff (1824–87), the physicist. They became lifelong friends and their later collaboration in the development of the spectroscope had outstanding consequences throughout the scientific world. It is sometimes said that Bunsen's greatest discovery in Breslau was Kirchhoff, but he had other triumphs to his credit. Here he isolated metallic magnesium electrolytically, analyzed the highly explosive nitrogen iodide and chloride, and developed what he termed "a volumetric method of very wide application," namely, iodometry. On the basis of his studies of the incomplete combustion of hydrogen-carbon monoxide mixtures, he had announced certain regularities which seemed to contravene the laws of mass action. A reworking of these experiments showed that these regularities were due to certain conditions which concealed the true state of things. Bunsen's real stature as a scientist was demonstrated when he freely admitted his error, a procedure which many have found difficult or impossible.

The chair in Heidelberg, which had been vacated by Gmelin in 1851, was still unfilled. It was hoped that only a recognized celebrity would be called, and both Bunsen and Liebig were proposed by the Heidelberg medical faculty. The philosophical faculty preferred A. W. Hofmann (then at the Royal College in London) or Remigius Fresenius of Wiesbaden as representatives of "practical chemistry." Liebig was negotiating with Munich and after about a year decided to accept the very favorable terms offered by the king of Bavaria. Bunsen, who had come to Breslau rather recently, declined to be considered at first and was thanked by the Prussian administration for his loyalty to his native country. It was hoped that the longer he stayed at Breslau the happier he would be. However, he was not feeling too well and finally acceded to urgings of the Baden authorities. He was appointed on August 6, 1852, with the promise of a new laboratory and the title and rank of *Hofrat* (Privy Councillor). The salary was fixed at 2700 gulden (one gulden equals about 25 cents) plus 400 gulden as allowance for rent until the completion of an official residence.

Bunsen taught and worked at Heidelberg from October, 1852, until his retirement at Easter, 1889. He was then 78. His accomplishments at this university, his achievements in both chemistry and physics, his fame as a trainer of eminent chemists, his eccentricities, etc., have been too often detailed to need any special discussion here. He died peacefully on August 16, 1899, at the age of 88, and is buried in the cemetery at Heidelberg, where he lies not far from his predecessor Gmelin and his successor Victor Meyer (1848–97).

The great Belgian chemist J. S. Stas (1813–91) summed up this useful life: "Le grand Bunsen, c'est le maître à nous tous, car tout ce qui est sorti des mains de cet homme, ces sont des chefs d'œuvres."

Little did Bunsen's friends know what lay in the future when they bade him farewell at Cassel. Though he even then showed promise, not even the most devoted of these young men could have dreamed that the young friend was starting on the road which was to take him to the greatest heights of the scientific world. Had they been able to anticipate such triumphs, would the cartoons have shown the group in mourning? Rejoicing would surely have been the theme of these affectionate testimonials.

⁴ Much has been published regarding Bunsen and his work. The most detailed account of his life, together with a bibliography of his publications and an extensive list of papers about him, will be found in LOCKEMANN, G., "Robert Wilhelm Bunsen," Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1849.

◆

"SCIENCE is an activity and not merely a body of facts. Throughout, the social implications of science, the powers that it puts into men's hands, the uses they could make of them should be brought out and made real."

● TRANSLATING FOREIGN-LANGUAGE PATENTS¹

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THE programs of this division have often contained papers on various aspects of patent work; they have also offered many papers on foreign-language problems. This discussion is probably the first on one of our programs to combine the two general subjects.

One of the topics in a symposium on foreign-language problems, arranged for the last meeting of the A. C. S., was: An Approach to Biochemical, Pharmacological, and Medical Terminology in French and German Chemical Literature. In a sense this may be considered parallel to this paper, for patent attorneys do not often make their own translations. It is the chemist who must learn the meaning of legal terms, and not the attorney who learns the relation of monoacetic acid ester of salicylic acid to aspirin. However, the parallel between these two papers cannot be carried too far; it is not a question, here, of extending the knowledge of one subject terminology over to another, but rather one of superimposing a second language or terminology, foreign to the chemist, on a nomenclature with which he is supposed to be thoroughly familiar. The results are usually confusing, sometimes unintelligible, and nearly always frustrating for the chemist. Why something "depends" instead of just "hanging"; why "plurality" has to be used instead of "some," or "several," or "a number of" is puzzling. The phrase in a claim: "at least one of a group consisting of copper, iron, and nickel" does not make sense, for these metals are not related chemically; and "a substantially evacuated transparent envelope containing an energy translating device" seems a particularly opaque way of describing an ordinary electric lamp bulb.

Moreover, although chemists are certainly accustomed to using long words and groups of words, the custom (not backed by any legal requirement, as far as we know) of writing each patent claim as a single sentence appears pointless. Certainly it adds nothing to the ease of understanding or of translating the claim.

If patents written English are confusing, how much more so are those written in a linguistically foreign language. The common quip, that all patents in English read as if they had been translated from German, is an exaggeration, even if only slightly so. Somewhat more hyperbolic is the statement that if a translation of a patent makes sense, it is a poor translation.

We have tried to point out a few of the problems of patent terminology in relation to the lay chemist, and, as already stated, foreign languages add even more twists and quirks to the maze. Moreover, differences in patent practice in foreign countries introduce additional complications. Even the term used for "patent" has its peculiarities. Nordic languages (including English) use "patent," and Slavic languages follow suit; its root meaning is "opened" (to the public). The Romance languages favor their own forms of "brevet," since a patent is a "brief." The Dutch "octrooi" came from Latin "auctori"; *i. e.*, the government "authorizes" the grant.

Pet foreign patent terms can be particularly troublesome when there are no exact legal equivalents, such as the distinction between "granted" and "issued," or "laid open for inspection" (for purposes of opposition).

Payne² gives a most valuable table of the following terms: inventor, assignee, filing date, granted, open for public inspection, issued, characterized in that . . . (before the novel matter in patent claims of certain foreign countries), example, priority, and claims. The languages included are German, Dutch, Danish, Norwegian, Swedish, French, Spanish, Portuguese, Italian, Polish, Czech, and Croatian. The names of the months are also given for the three Slavic languages.

Some legal terms of patent interest are included in Austin M. Patterson's familiar German-English and French-English dictionaries for chemists. The late Arthur Worischek, a patent attorney, was noted (among numerous other accomplishments) for his knowledge of many foreign languages. He contributed a "plurality" of patent terms to Regen & Regen, "German-English Dictionary for Electronics Engineers and Physicists." The German-English-French and English-German-French volumes of Thali's "Technisches Wörterbuch" also contain a selection of patent terms. Again, the many available legal and commercial dictionaries from foreign languages into English have patent terms scattered through them. These are not specifically so designated as a rule, unless the term "patent" or "claim" appears in the term being defined.

In the actual process of translating, the chemist-translator should hew to the same wavy line of indefiniteness and apparent vagueness which is laid out in the original text. The natural tendency of any scientist to be precise has to be suppressed, and vagaries of

¹ Presented before the Division of Chemical Literature at the 127th Meeting of the American Chemical Society, Cincinnati, March, 1955.

² J. CHEM. EDUC., 25, 389 (1948).

chemical nomenclature or even of definition have to be followed in preparing a translation which aims at the straightest possible parallelism from a legal point of view. It is not necessary (for example) to point out to an attorney that there is a great deal of difference between the use of "a" and "the" in a legal text; but translators of technical-legal matter often need to have this emphasized. This is especially true in translating from the Slavic and certain Oriental languages which have no equivalent for either "a" or "the."

Thus, at one and the same time the translator needs to be both indefinite and precise, and in just the manner that is most difficult for him. He must hew to the wavy line in using the technical terminology with which he is familiar, and in which he is trained to undeviating due-west linearity when heading west. On the other hand, he must at the same time hew exactly to a straight line of unfamiliar legal terminology which often reveals no sensible meaning to his frustrated vision. Why, for instance, does the subject of a patent "relate to" something, instead of simply being "about" it? Or why, again, is earlier work in a certain field cited in a patent text as "prior art"? In translating patents, moreover, the correct rendering of such terms is complicated by the fact that their legal equivalents in foreign patents are not always linguistic equivalents as are the accommodating pair "example" and "Beispiel." Thus, a knowledge of English-language patent terminology and, it is to be emphasized, of its correct legal use, is quite necessary for the translator. There has been many a discussion among technical translators as to whether the French term "résumé" is or is not correctly translated as "claim," quite apart from the legal significance of the term as used in a patent. The same argument might arise about the correct rendition of the Dutch word "conclusie."

There is a crumb of comfort for the chemist-translator. A patent is a bargain; in return for monopolistic privileges granted by the government (U. S. or foreign) the patentee tells the world his treasured secret. Legally a patent specification is a "disclosure" and everybody knows it is written to reveal only as much as the government demands, no more.

So the business of prosecuting a patent application is a battle of wits between the examiner (seeking the best bargain for the government) and the attorney (seeking the most for the least, to make his client happy). Exactly as with the Star Spangled Banner over Fort McHenry, the resulting wind of controversy "as it fitfully blows half conceals, half discloses."

If the two portions (half is purely imaginative, not mathematical) do not strictly coincide in the translation and the original, the difference has as good a chance of favoring as of disfavoring the translator's client. So the objective is to allot vagueness and precision exactly where they belong, but there is no profit in worrying over small deviations from perfection.

Patent specifications have examples; we will offer a few here, taken from foreign-language patents. Among other points, they illustrate the translator's lack of

freedom to inject personal knowledge into translations. Even an incorrect or untrue statement must be translated as is, assuming that the client's expert knowledge will recognize error; and typographical errors should be indicated in a form such as "(error for—?)," leaving final interpretation to the client.

Example 1. When a specification says "917 million micrograms" instead of "917 grams" there is probably a reason; go and do likewise.

Example 2. Such an expression as "0.1 N Kalilauge" is likely to involve intentional vagueness as to exact composition or purity to offset the precision as to concentration; better render it "caustic potash" rather than formalize it as "KOH."

Example 3. Beware of the difference between "basic" meaning "fundamental," and meaning "alkaline." "Base material" is safe for "grundmaterial" whereas "basic material" would imply too much.

Example 4. Occasionally chemical patent terminology violates the translator's sense of propriety without giving him a sure guide to the correct term. If a German patent says "propin" and offers no evidence that it means "propyne," the translator can do no more than raise the question; *e. g.*, by the rendering "propin (propyne?)." But if the patent says "methyl acetylene (propin)," then he can safely say "propyne."

Example 5. In biochemical patents the nomenclature trouble sometimes arises from differences between European and American terminology, and sometimes from use of obsolete or obsolescent names. Thus, a patentee may insist on referring to *Bacterium aceti* instead of *Acetobacter acetis*. The translator's cue is to follow suit. If he knows his client's interests and temperament well enough to feel safe he may add "(synonym *Acetobacter acetis*)," but he is not free to take greater liberties with the terminology he finds.

Example 6. In German technical literature, outside of patents, "Fachmann" means anyone engaged in the practice of a "Fach" which originally meant any trade or occupation (more or less excluding the ancient three "estates" of law, medicine, and the clergy). As science and technology advanced, any branch of either became duly recognized as a "Fach," and the lowliest cleaner of messy vats is a "Fachmann" (at least in his own view). So is the Nobel-prize winner who gave the instructions which messed up the vats; so are all the practitioners in that branch of knowledge, between the top and bottom levels. In German patent literature, however, "Fachmann" almost always means exactly the same as the U. S. patent phrase "one skilled in the art."

All patents have claims, but this discourse has none. It cannot claim erudition and declines to risk claiming validity. If in following our advice a translator hews to a wavy line of vagueness and learns too late that the valleys are where the crests belong, we accept no responsibility. We have enough trouble with our own valleys and crests. We hope these remarks will help a little here and there in unsnarling problems of waves and parallels, but we make no promises.

A CURRENT STABILIZER FOR LABORATORY ELECTROLYTIC PROCESSES

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IN MANY laboratory electrolyses, the chemist may wish to maintain a fairly steady current although the resistance of the system, and thus the necessary voltage, may vary widely or undergo rapid fluctuation. The circuit shown, though not truly a constant-current supply, can maintain currents of up to 400 milliamperes to within a few per cent, even when voltage changes in excess of 100 volts are necessary. The unit is versatile, simple, and inexpensive, and thus should be useful in many college laboratories. Our model could be reproduced for about \$30.

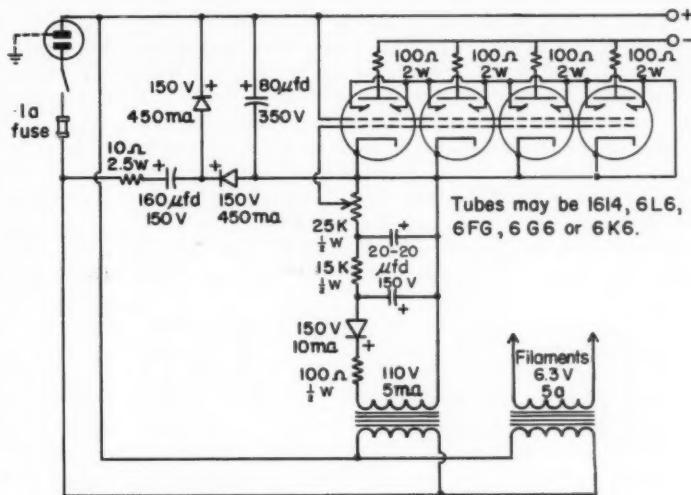
Current stability is obtained by taking advantage of the high plate resistance of a pentode-type vacuum tube. The circuit employed is shown in the figure. The same result could be obtained, of course, using a high-voltage supply and a large dropping resistor; however, to obtain equivalent current stability the supply voltage would be from 1000 to 2000 volts and the dropping resistors would have to dissipate up to 300 watts. In contrast, our unit operates at maximum values of 300 volts and 120 watts.

The voltage-doubler power circuit operates directly from the power line. If one terminal of the load is to be at ground potential, it will thus be necessary to insert the power plug "right side up," with the proper terminal to the ground side of the line. At some extra cost, this situation could be remedied by using a one-to-one isolation transformer.

For maximum current, four type-1614 tubes are used in parallel. At currents up to 320 milliamperes the cheaper type-6L6 tubes could be substituted. Under 80 milliamperes somewhat steadier operation is obtained by removing all but one tube. At low currents (10 milliamperes or less) a single, low-power tube such as a 6G6, 6F6, or 6V6 gives slightly improved control. This substitution may be made without circuit alteration, as base connections on the tubes mentioned are equivalent.

¹ Present address: Gustavus Adolphus College, St. Peter, Minnesota.

² Present address: Metallurgy Division, U. S. Naval Research Laboratory, Washington 25, D. C.



In three different laboratory applications this instrument has performed very well. Response to resistance changes is for practical purposes instantaneous, and the current stability achieved frees the operator of the task of constant adjustment of supply voltage.

ACKNOWLEDGMENT

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Performance of Current Stabilizer Circuit

	Load resistance, ohms	Load voltage, volts	Load current, milliamperes
Single 6F6 tube, set for six milliamperes	0-1000	0-6	6.2
	1500	9.2	6.1
	5000	30	6.0
	10,000	59	5.9
	15,000	87	5.8
	20,000	112	5.6
	30,000	162	5.4
Four parallel 1614 tubes, set for 300 milliamperes	50,000	250	5.0
	0-56	0-17	310
	75	22.5	300
	250	72.5	295
	350	100	285
	500	132	265
	650	156	240

CATALYSTS AND REACTION PRODUCTS¹

GERRIT VAN ZYL

Hope College, Holland, Michigan

RECEIVING an award such as the Scientific Apparatus Makers Award in Chemical Education tends to make one wonder why, and on what basis, he was selected for such a great honor. Why was not any one of a host of others, more deserving, so favored? In such matters we have nothing to say, and can only modestly and gratefully accept the choice of the committee who have made the decision. It is a heartwarming experience to realize that one has so many friends among his former students and his contemporaries in the field of chemical education in all parts of our country, who believe that his service to chemical education warrants this honor.

If I have been able to inspire some, it is only because others have been an inspiration to me. My first impulse to study chemistry and to become a chemist or a teacher of chemistry was activated, in 1914, by Dr. Almon T. Godfrey, professor of chemistry at Hope College from 1909 until his death in 1923. Professor Godfrey was a physician, who in his later years devoted most of his time to the teaching of chemistry. A stern teacher and a strict disciplinarian, he nevertheless exhibited a dry sense of humor, and commanded the respect of his students. His teaching constantly emphasized the importance of fundamental principles of thoroughness, honesty, and accuracy. Students who exhibited a genuine interest in chemistry and who met his exacting standards were rewarded with praise, which was the more valued because it was sparingly given.

My interest in chemistry was further intensified by Hope's professor of biology, Dr. Frank N. Patterson, who was as much a biochemist as he was a biologist. It was his enthusiasm and his research spirit which captivated me.

To my university professors in the graduate school I am also greatly indebted. To Dr. Alfred L. Ferguson of the University of Michigan, under whom I worked for my Ph.D. degree in physical and electrochemistry more than three decades ago, I owe what I have learned of patience and persistence, and from him also I learned that a chemist must learn to get along with people as well as with molecules. My sincere appreciation is extended to Drs. H. H. Willard and F. E. Bartell who are still active among us, and to the late Drs. Moses and Gomberg and S. Lawrence Bigelow and many others.

Finally, for the success of our students I must pay tribute to my colleagues: Professors Harvey J. Klein-

heksel and Theodore L. Vander Ploeg who have so faithfully served as devoted teachers for many years, to my fellow faculty members in other departments, and especially to our president, Dr. Irwin J. Lubbers, who is a sympathetic and cooperative administrator interested in every department project.

As a "penalty" for receiving this award, I am supposed to say something about the teaching of chemistry. But what? It is not my purpose to discuss textbooks, course content, methods of teaching, or laboratory technique. These are all extremely important but they have been fully discussed by the previous recipients of this award: Dr. Lucas, Dr. Hildebrand, and Dr. Kirk, and by many others. Nor is it my purpose to make comparisons between the colleges, the universities, and the technical schools which are all a necessary part of our educational system. If I did so I would undoubtedly be very unscientifically biased, for except for a few days as a substitute teacher of Latin and algebra in high school, and three years as a graduate assistant, my teaching experience has been in the small, liberal-arts college.

Rather, I would like to emphasize a few of the stimuli and influences in any good chemistry department and program which are essential in motivating both the student and the teacher to become better chemists and chemistry teachers. These are important for the undergraduate program in a small college or a large university.

STUDENT AND TEACHER SHORTAGE

That there is need for good undergraduate chemistry teaching and for training of high-school chemistry teachers is evident from a number of recent articles. Many of our magazines such as *Time*, *Newsweek*, *Chemical and Engineering News*, the *Journal of Higher Education*, and THIS JOURNAL are replete with editorials and articles decrying the need for more high-school and college students in chemistry, more chemists with executive and research ability, and more and better teachers of chemistry. The colleges are dependent on the high schools, and the graduate schools on the colleges for their source of students.

Three hundred and ninety Iowa high schools replied to a questionnaire, sent out by James W. Kercheval of Iowa State Teachers College, to find out "Why Chemistry Is not Taught in More High Schools." Of the 390, 139 offered chemistry either every year or in alternate years. The remaining 251 do not offer chemistry. The reasons given for dropping chemistry are: (1) The parents and students are not demanding it because they do not see sufficient practical or general educational value in it; and (2) the school has no one in its employ

¹ Address presented on receiving the Scientific Apparatus Makers Award in Chemical Education, before the Division of Chemical Education at the 127th Meeting of the American Chemical Society, Cincinnati, March, 1955.

qualified to teach it. In the fourth annual report of the National Science Foundation it is estimated that the demand for high-school science teachers over the next decade will increase by 2300, and that the teacher shortage may be expected to become still worse and will extend to the colleges and universities.

An anonymous contributor to the January 31, 1953, *Chemical and Engineering News*, in "Don't kill the goose that lays the golden egg," suggests that the lack of interest in science in the high schools, and the lack of teaching manpower can be remedied by the "judicious use of financial rewards." This might decrease the number of more capable teachers who are siphoned off into better paying jobs in industry and encourage students to enroll for the relatively more difficult science education. But this alone is not sufficient. The public and the high-school students must be made aware of the tremendous importance of science in the world today.

The National Research Council, the National Academy of Science, the American Chemical Society, and many other scientific organizations and educational societies are making a concerted effort to cope with this increasing need to improve the quality and quantity of teachers in the secondary schools and colleges. They are "making an intensive effort to identify and encourage various remedial measures which can be taken both on a local and a national scale by those who participate in or benefit from the profession of science." Enthusiastic reports of the success of the conference for high-school teachers held at Kenyon College last summer, sponsored by the National Science Foundation and the Division of Chemical Education, are proof that there should be more of them in various areas. The local sections of the American Chemical Society should take a still more active part by paying the entire expense to these conferences of more teachers within their territory. The inspiration received by those who attended is sure to be reflected in their students. The First Annual Conference of College Chemistry Teachers, held at the University of Wyoming for five weeks, was a stimulating positive catalytic influence on the 125 or more who attended. I was privileged to have an active part on the program. It was an unusual opportunity to hear and become acquainted with such leaders in science as Bailar, Elving, Swift, Daniels, Hildebrand, Libby, Seaborg, Vanderwerf, and others. The impetus which these teachers of college chemistry received is surely being transmitted to their classes.

All such steps are excellent, but the most important single step in the remedying of the great shortage lies in the improvement of the quality of the chemistry education program at the undergraduate college level. Here the interests of young people are aroused to the point that they choose a life work. The key decision to become a chemist or a chemistry teacher—who in turn will stimulate others to be chemists—is made during these years.

Hence, it is very important for us to rethink not only the classroom activities and methods, but also the entire series of activities in which we engage that can make

a real impact upon our students, and even upon ourselves.

To touch concretely upon these activities without reference to my own experience is virtually impossible; yet to dwell on what I know best seems not only immodest but also improper. Caught in this dilemma, I am forced to report honestly as a scientist the conclusions which have been reached, based upon the evidence at hand. And if my illustrations seem to be drawn rather largely from the liberal-arts college, and especially from my own college, I believe similar examples could be cited for liberal-arts colleges and undergraduate programs in universities all over the country.

THE TEACHER

In any college there are numerous influences which have a catalytic effect on the character, thinking, and the development of the career of the student. By far the most important is the guiding influence of the teacher. Harry F. Lewis of the Appleton Institute of Paper Chemistry, who has a warm spot in his heart for the liberal-arts college, has said: "The professor who cares will be an important part in the student's adjustment to life in general as well as to chemistry in particular." Those who are teachers of our nation's youth have great obligations to fulfill. In four short years we cannot expect to do much more than to induct a student into some knowledge of the nomenclature of his subjects, and into their highest generalizations, so that he may be prepared, as genius and opportunity permit, to devote himself to some lifework in which he may investigate the mysteries of some single branch of that great body of scientific or philosophical investigation.

Every teacher, whether in the high school or college or in the graduate school, has in mind a number of young men and women whose energy of activation he hopes he has raised above that of the average student. He hopes that the impact of his personality on the students majoring in his department is such that they have a burning desire to seek higher levels of education and to become leaders in their professions. The teacher is a most effective catalyst if he is modest, friendly, unassuming, and an inspiration to his students. I have known some teachers who exert no such influence at all. In fact, there are some negative catalysts who are interested only in their pay checks and should be weeded out of the profession.

The teaching emphasis should be on the importance of getting a good foundation of thoroughness, honesty, and accuracy. In addition, the teacher should instill a fine spirit of worth-while living in the students. Such men are needed in science more today than ever before because science is rapidly taking the lead in world affairs. The loyalty of such men and women to their Alma Maters and to their professors, and their excellent performance as graduate students, teachers, and chemists will be living examples of the superior work of their teachers and their influence upon the lives of their students. It is our duty as teachers and mem-

bers of the Division of Chemical Education and of the American Chemical Society to discover the talented, hardworking, ambitious students, and to encourage them to become the future teachers, doctors, research workers, and executives in industry.

SEARCH FOR TALENTED STUDENTS

To build a strong chemistry department it is necessary first of all to insure a supply of good students. It is up to us to find the young men and women who are to become the reactants in this catalytic process of education. Some may come to us inspired by some high-school teacher like Bill Lane, whose activities are recounted in the January issue of the *Reader's Digest*. Others come expressing only a casual interest in chemistry, medicine, or physics. We search the entrance applications in the admissions office and glean from them the list of promising students. They are counseled and guided during their freshman and sophomore years. Some drop by the wayside or are directed to other courses for which they have more aptitude. Others are encouraged to pursue medicine or medical research, and the remaining few may want to specialize in chemistry. We must look for and foster in them the personal characteristics of integrity, industry, ingenuity, initiative, judgment, cooperation, personality, poise, leadership, perseverance, and enthusiasm. We must induce the educational characteristics of scholarship, scientific attitude, comprehension, laboratory technique, and report writing.

THE CHEMISTRY CLUB

But students once obtained must be stimulated to maintain their efforts. Groups of students with a common interest must be organized into clubs or societies, such as chemistry, physics, mathematics, and pre-medical clubs. These are essential for increasing the enthusiasm of the student. Many of us well remember the days when the science club consisted of only five or six members or less, but all of them were dedicated to the pursuit of science. There are countless examples of such groups growing to a membership of from 20 to 30 or more, and eventually becoming an affiliate chapter of the American Chemical Society. In the Chemistry Chapter at Hope College, the membership consists of seniors and juniors and the highest-ranking members of the sophomore class who plan to make chemistry their profession. All students are, however, invited to attend the meetings. The senior students are expected to present a one-hour lecture at least once. The group attends the Kalamazoo section meetings of the American Chemical Society even though the meeting is held 50 or more miles away. Fortunately, we are now included in a subsection of the Kalamazoo section which meets alternately at Hope College and at Calvin College in Grand Rapids, Michigan, 25 miles away. Our students' enthusiasm for chemistry has been boosted enormously after they have heard such men as Harry L. Fisher and Alsoph C. Corwin.

Another stimulation comes from at least one trip to

an industrial research laboratory and plant, such as the Dow Chemical Company, General Mills, Parke-Davis, or the Standard Oil Company of Indiana. The annual program of the affiliate chapter includes one or more open house meetings to which high-school students and citizens of the surrounding communities are invited. An interesting array of special equipment is displayed, with the better students performing experiments in each laboratory. All of these events are excellent stimuli to the student's interest in chemistry.

SCHOLARSHIPS AND FELLOWSHIPS

Students can also be encouraged by provision of greater rewards for outstanding performance. Scholarship awards, granted on the basis of ability, initiative, personality, and needs, are good incentives to better scholarship and increased interest. During the past year, 14 of our undergraduate students received scholarships ranging from 150 to 500 dollars, from funds contributed by the Standard Oil Company of Indiana, the Johnson Foundation, the Dow Chemical Company, and the du Pont Company. Other colleges receive similar grants from industries. General Motors has started a two million dollar annual scholarship program, and Union Carbide and the Standard Oil Company of New Jersey have extended their programs to include smaller schools as well as the universities. It is an encouraging sign that industry as a whole is beginning to recognize more and more the importance of the small, liberal-arts colleges in the training of scientists.

A prize, upon graduation, to the most outstanding student in the department leads to keen competition. In 1926 such an award was established at Hope College in honor of my predecessor. All of the 32 seniors who have won this prize in the past have also received assistantships or scholarships in various graduate schools. Twenty-four of the 32 have obtained the Ph.D. degree. Five obtained the masters degree and three are still working for advanced degrees at the University of Illinois, Massachusetts Institute of Technology, and the University of California at Berkeley. Nine of these graduates are or have been university or college teachers, one is a college president, and the rest are industrial research chemists or research directors. A number of them are present at this meeting and included among them is the chairman of the Division of Chemical Education.

UNDERGRADUATE RESEARCH

In any laboratory there should be a research project carried on by the faculty or the faculty and students. This matter of undergraduate research should have more emphasis. It is my firm conviction that the fundamental courses in chemistry and in other fields of learning should not be sacrificed or replaced by the research program. In fact, an undergraduate research program, though desirable, is not a *must* in the undergraduate school. However, the faculty from the head of the department down to instructor should have the research attitude and continually stress the research

approach in their teaching; and if possible engage in some projects of their own, however small, and thus motivate their students by their example. How can you expect to impress the importance of laboratory work on the minds of your students if you never touch a test tube yourself? The teacher should be seen in the library frequently, delving into *Chemical Abstracts*, Beilstein, the periodicals, and the most recent books published in his field. No student from freshman to senior should ever be discouraged from performing an experiment by a modified or an entirely new method, or devising a new experiment which he may perform under proper supervision. This is research on a small scale. It does not seem to me to be necessary that all senior chemistry majors including premedical students should be required to undertake a research project. If they have been properly stimulated, they will want to do so. At the end of the junior year it is not difficult to determine who of your students have the interest and ability to do research. If funds are available, a student may be given a grant for summer research. The work can be continued during the senior year as a part of a regular advanced course or a course in special problems. Then during the following summer, after graduation and before graduate school, a student may become a coauthor with his professor of an article in a chemical journal. By this time he will have such a genuine interest in your research program that he will desire to return for a summer after his first year of graduate work and possibly the second and the third. It has been my pleasure to have several such men. Dr. Eugene Van Tamelen, a Harvard graduate, worked in our laboratories for four summers and has since been on the organic chemistry staff of the University of Wisconsin for five years. Dr. George Zuidema, who received his M.D. degree from the Johns Hopkins Medical School, likewise worked in our laboratories for four summers. Others who have worked with me for two or more summers at research projects are Dr. Paul Cook from the University of Illinois, now teaching at Albion College, Dr. Earl S. Huyser now a post doctorate at the University of Chicago, Paul R. Kroman a third-year student at the University of California at Berkeley, John F. Zack a third-year student at the University of Illinois, Robert Langenberg at the University of Vermont, and Robert Schut at Massachusetts Institute of Technology. I know of no experience more thrilling than to work with a group of four or five such men during the summer months. Many other liberal-arts colleges have more or less extensive research programs. The research activities of Augustana, Monmouth, Oberlin, Reed, Wabash, Wooster, and many others have been presented at some of our conferences. Grants for such programs are available from the Research Corporation, the National Science Foundation, other similar foundations, and a growing number of chemical suppliers and manufacturers. As a result many articles have been published in scientific and educational journals, and many teachers and students have been inspired to pursue their work with greater zest and vigor.

The value of the undergraduate research program has been the subject of much discussion at meetings of the Midwestern Association of College Chemistry Teachers, at Appleton, Wisconsin, and at Grinnell College. Twenty-eight colleges were selected to take part in an undergraduate research conference at Washington and Lee University under the sponsorship of the National Science Foundation and the Division of Chemical Education. The subject was again thoroughly discussed at the First Annual College Chemistry Teachers Institute, held at the University of Wyoming. I am sure that these conferences were as inspiring to others as they were to me. Similar conferences have been held elsewhere. They should be continued and increased in number. Such experiences are most stimulating for the teacher, whose activation energy must also be raised at times. The catalyst which has been poisoned or deactivated must be rejuvenated.

It has been argued on various occasions that outstanding ability in research and outstanding success in teaching do not go together—that we cannot expect both in the same person. Dean Lawrence H. Snyder of the University of Oklahoma said: "I do not believe this for a minute. It is true that an inspiring teacher is often justified on his teaching ability alone. But I am convinced that the two abilities can be of the highest order in the same man or woman. I wonder if the belief that they should not be expected to coexist has not sometimes been used as an excuse on the part of an individual who has reached success in one field for his lack of industry in the other."

In a small liberal-arts college one must first, of necessity, be a teacher. But a limited research program can be established even in a one- or two-man department. The usual reasons given for not having such a program are lack of time, lack of money, lack of equipment, lack of library facilities. It is more likely due to lack of ideas or unwillingness to start. All of these obstacles can be overcome to a large extent. There is always some time left if a man is not a clock-watcher or is not loaded down too much with administrative duties. He may be spending too much time on the eternal problem of satisfying the exponents of general liberal education. In their desire for education for all the students, they ignore the fact that a limited amount of specialization is necessary for the superior student. Money is available from foundations, corporations, and from industries if you have a problem of any significance. Every laboratory has at least the usual equipment for course work. The research program will increase the demand for new equipment and the administration will grant it only if you create the need. Sometimes your ingenuity is tested by the necessity for building your own equipment. Many of your graduates, teaching in the universities and working in research laboratories, will gladly cooperate with you when there is need for an ultraviolet or an infrared analysis. The small college usually does not have an extensive chemical library, but many of the difficulties can be overcome if one has a full set of Beilstein, the complete

indexes of *Chemical Abstracts*, and the American chemical journals. In this day of rapid transportation a trip to a university or large city library, where one can spend a day or two in library research, is not out of the question. Photostatic copies of articles are readily obtained, or better still a relatively small investment in a microfilm reader will enable one to read any published article for approximately one dollar. Ideas for advancing research will come with overwhelming rapidity when one once starts to work. But *you must start*. Ideas may be obtained from textbooks, the chemical literature, conversations with friends and former students, or from the active researchers one hears and meets at the local and national meetings of the A. C. S.

THE ALUMNI

It has always been my contention that 90 per cent of a college's reputation is due to the contributions and achievements of its graduates. It is therefore extremely important that the college should keep in close contact with them, and not lose sight of them after they receive their B.A. degrees. The alumni can be a great stimulating influence on the faculty and students. At Hope, in addition to all of the general alumni chapters located in various parts of the country, there is a Science Alumni Chapter, separate from the parent organization. Its permanent secretary is a member of the science department. Any science graduate is automatically a member. A questionnaire is sent out every five years and records are kept of date of graduation, scholarships or fellowships received, place of internship, degrees earned and where, where practicing medicine or where employed, and a list of publications.

The officers of the Science Alumni Chapter include a president, vice-president, secretary, and central committee of 20 prominent alumni in the various fields of science. A few years ago this committee initiated a drive and raised \$15,000 for scientific equipment and library periodicals. A number of prominent alumni have returned to our campus, from time to time, to lecture to our students on their interests in chemistry. Many students have come to our college because of their influence. Dinner meetings are held concurrently with meetings of the A. C. S. or other scientific organizations. When such men and women are inspired to loyalty there is bound to be progress on the local campus.

THE PRODUCTS

These activities which have been mentioned are but a few of the many which lead to the formation of useful products. The material is crude. Perhaps it is once recrystallized. It is a great source of encouragement that the graduate schools of our universities and the industries willingly and graciously accept the products which we have turned out for further refinement.

The evaluation of the "work of our undergraduate institutions as progenitors of our professional chemists, to the extent that these are represented by the Ph.D.'s and the Sc.D.'s in chemistry" is published in detail in the Steelman Report to the President, the Trytten

"Report on the Baccalaureate Origins of the Science Doctorates," and in the recent book by Knapp and Goodrich. Some have made a more outstanding record than others, but others seem to have furnished only a few Ph.D. candidates and some apparently made no effort at all in this field. These should be encouraged to do so. I am sure that many present here have had experiences like ours. We recall with pleasure the many graduates who have received assistantships, scholarships, or fellowships at some 50 universities.

One is reminded of the 32 students who have been candidates for a higher degree at a single Midwestern university. All but one of the 32 obtained at least the masters degree. Twenty-one continued and received the Ph.D. degree. Two are high-school teachers and 13 are or have been university or college teachers. Four of the 32 are still working toward the Ph.D. degree. We are especially gratified that eight of our former students received their Ph.D. degrees during the past year. The record of the hundreds of medical doctors who have graduated from the small colleges is also a source of satisfaction.

There is a constantly growing need for increasing the quality as well as the quantity of scientists in America. It is from these men and women in our colleges that a genius occasionally emerges. We have all heard the cry, "We are losing the technological war," or "The U.S.S.R. is turning out 50,000 scientists a year." The words "scientist" and "technician" are sometimes used interchangeably. There is no denying the need for technicians. The technician is a craftsman, the scientist is an artist, a man with a vision. Any person can learn to be a technician, but who can learn to have vision? Society does not sufficiently encourage the natural development of scientists or original thinkers in many fields. What if there had never existed an Einstein, an Oppenheimer, or a Pauling? Are we perhaps discouraging such men from being pioneers of knowledge? Does our society perhaps inhibit men who think in novel terms and ostracize those who dare to differ, so that, if they were to choose their careers over again they would choose to be *plumbers*?

Do we in our laboratories, classrooms, and offices provide the stimulus that is likely to muster and breed the real scientist? This is our challenge. The activities and procedures I have suggested may be a few ways whereby we can improve our chances of finding and developing those scientists who have a thirst for knowledge, a creative imagination, and a sense of integrity. There are many more. That is why being a teacher of chemistry—in spite of the rather meager financial compensation—is the most rewarding and exciting vocation any man can find.

Teaching is creative work, with its basic materials the minds, the hearts, and the ambitions of impressionable youngsters who desperately want and need proper guidance. Teaching has only one motive—service to mankind.

I for one am happy to have been of service, in a small way, to the students of a liberal-arts college.

● LOW-TEMPERATURE ABSORPTION SPECTROSCOPY

(Cryoabsorption Spectroscopy)

FREDERIC L. HOCH

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IMPROVEMENTS in instrumentation for the dispersion and measurement of radiations have been continuous over the past few decades. The increasing availability of such apparatus has facilitated the increasing range of application of absorption spectroscopy. Not as much attention has been given to the possibilities of treating the radiation-absorbing materials themselves to produce spectra of increased information value. Reduction of temperature often results in changes in absorption spectra. Spectra of cooled materials may exhibit increased absorption and detail, and chemical structures unstable at ordinary temperatures may cause measurable absorption. Very low temperatures may be produced and maintained by apparatus intrinsically capable of simplification for wide use, and such techniques already have been applied in a number of investigations.

Cryoabsorption spectroscopy is the study of the absorption of electromagnetic radiations by materials which are at low temperatures. The effects of temperature upon the colors of substances—thermochromic effects—were noted by Brewster in 1831 (1), but J. Becquerel in 1907 (2) first reported changes in absorption spectra of substances at low temperatures, although Liveing and Dewar had visually observed the spectrum of liquid oxygen earlier (3). Subsequent investigations have dealt with the spectral range from the infrared to the ultraviolet, and recently the vacuum ultraviolet (4) regions. Temperatures have extended from that attainable with solid carbon dioxide—about 195°K.—to that with liquid helium—about 4°K.

PHYSICAL BASIS

Reducing the temperature of many substances produces characteristic changes in their absorption spectra: increase in absorbance of bands, reduction of their half-band width, changes in the number of bands or lines, and shifts in position of absorption maxima. The first three phenomena increase the informational utility of these spectra both for qualitative and quantitative purposes. However, the physical factors producing such spectral alterations are complex and interrelated, and may act in opposing directions. Not all materials exhibit spectral deviations at low temperatures, and the spectra of structurally similar compounds may show them to varying degrees; a compound may itself show cryoabsorption effects

varying with the degree of hydration of a solid film or with the solvent used (5, 6). *Intramolecular* and *intermolecular* effects upon the absorbing structures may be considered.

The primary effect of the reduction of temperature upon radiation-absorbing systems is an *intramolecular* one: the depopulation of thermally excited energy levels in accord with the Boltzmann relationship. The lowered probability of such energy transitions reduces the number and absorbance of lines or bands depending on thermal excitation, while the increased population of the lower energy levels causes increased absorbance in the corresponding spectral bands or lines. This narrowed range of energy levels from which spectral features arise produces a decrease in the width of bands. A further reduction in half-band width is due to the decrease of the Doppler effect in proportion to the square root of the absolute temperature.

Intermolecular effects of reduction of temperature follow upon this primary effect. The depopulation of thermally excited translational, rotational, and vibrational energy levels reduces the randomness of orientation of the molecules of the absorbing system, and thus the randomness of intermolecular electrical and magnetic forces. Such increases in field strengths cause "internal" Stark and Zeeman effects upon absorbing structures; bands or lines are broadened, split, and shifted, and their absorbance is decreased. These spectral alterations are most strikingly seen when intermolecular fields undergo abrupt changes in symmetry of orientation, which occur at characteristic temperatures of transition of state, or at temperatures associated with transitions of crystal structure in the solid state. However, the effect is recognizable within a single state of crystal habitus, where thermal contraction is a physical indication of increasing internal field strengths, and where spectral changes are observed. Other intrastate spectral shifts may be due to the displacement of equilibria between molecular isomers of different energy status; as temperature is lowered, configurations requiring the least energy for their maintenance predominate.

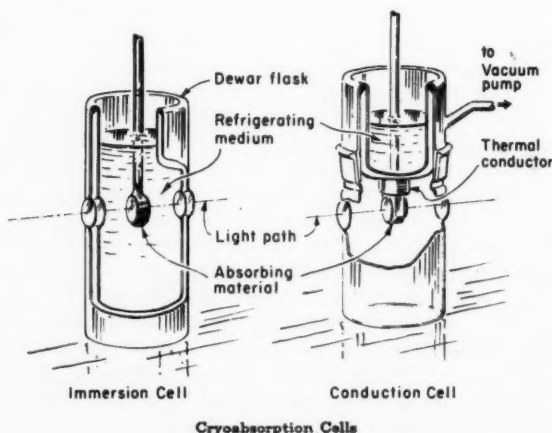
In crystals, where vibrations of the lattice absorb characteristic low-energy frequencies of radiation, a special intermolecular effect is noted in cryoabsorption spectra. These vibratory modes may be coupled additively or negatively with intramolecular modes,

Effects of Low Temperatures upon Features of Absorption Spectra

	Changes from spectra observed at ordinary temperatures				
	Absorbance	Band position shift	Half-band width	Band symmetry	Number of bands
Intramolecular effects					
Population of ground state alone	+	+	-	0	-
Reduction of Doppler effect			-		
Intermolecular effects					
Increase in field strength	-	+			+
Crystal lattice absorption					+
Lattice-molecular coupling	±	+	+		+
External effects					
Christiansen filter effect		+		-	
Multiple internal reflections	+				
Contraction of absorbing medium	+				

Presence or increase = +; decrease = -; no change = 0.

increasing spectral details. However, reduction of thermal energy to very low values allows population of only the ground energy state of the crystal lattice, and spectral detail may again be reduced. Low temperatures in crystalline substances may thus cause any combination of variations in absorbance, position, number, and contour of bands. In powdered or microcrystalline systems anomalous variations of light scattering with wavelength of incident radiation may also alter the contours of absorption bands (Christiansen effect) (7), while multiple internal reflections may produce an increase in effective optical depth with resulting increased absorbance (8).



The physical changes producing cryoabsorption effects in absorbing systems may thus act in opposing directions, the net effect being the resultant of these actions. This may explain the variations in cryo-

absorption effects among structurally similar compounds. A summary of the determinations of cryoabsorption spectra is presented in the table.

APPARATUS

The most immediate practical problem of cryoabsorption spectroscopy is the design of cryoabsorption cells which combine suitable optical properties with an effective cooling system. A number of cells have been designed, their simplicity approximately proportional to the desired absolute temperature. They are of two general classes (see the figure): (a) *immersion* types in which the absorbing material and the refrigerating medium both lie in the optical light path (9); and (b) *conduction* types in which only the absorbing material is in the light path, and where refrigeration is maintained by thermal conduction (10). Immersion cryoabsorption cells are usually simple, but are applicable only for spectral regions where the absorption of the refrigerant does not interfere. Control of temperature and wider spectral range are assets of conduction cells. Their construction, however, poses more problems, one of which is the nature of the junction between the thermal conductor and the optically clear and flat windows. This union must maintain its optical properties and withstand repeated shifts from low to normal temperatures, differences in contracture of its elements, vacuums, and solvents—a not inconsiderable demand.

Specimens have been prepared for cryoabsorption studies in solution or in solid state. Eutectic mixtures which remain fluid or vitreous at low temperatures have been used as solvents (11). Solid materials may be spread in thin films over clear surfaces or mounted as single crystals directly on holders which orient crystal axes for the observation of polarized cryoabsorption spectra (12).

APPLICATIONS

Cryoabsorption spectra have been used in studies of (a) atomic and molecular structure, (b) solid state and crystal structure, (c) monomolecular chemical reactions, and (d) unstable molecules and configurations.

The most extensive application has been in the theoretical interpretation of spectra for the elucidation of atomic and molecular structures. The rare earths have been so studied intensively; the shielded 4f electrons of these elements give rise to sharply defined absorption spectra at ordinary temperatures, and reduction of temperature with its further removal of external perturbations and the magnification of intermolecular Stark and Zeeman effects produces spectra of detail sufficient for analysis of energy levels. Changes in the spectra of rare earths at the temperature of liquid air were first reported by J. Becquerel (2), who noted that the increase in resolution produced absorption lines comparable in detail with those of metal vapors. The same investigator (13) observed characteristic cryoabsorption effects at the temperature of liquid hydrogen and the effects of temperature upon

absorbance in the direction of crystal axes. Further studies by Freed (14), Spedding (15), and others (16) have given information on atomic structure, the influence of neighboring ions, and the magnitude and symmetry of electrical fields in the crystals of the rare earths.

The cryoabsorption spectra of molecules may reveal energy transitions obscured in spectra at ordinary temperatures. Solids of ordinarily gaseous elements (17), salts of heavy metals (18), halogens (19), and organic molecules have been studied. Among the latter group, benzene in its three states was among the first investigated (20); the fundamental absorption frequencies in the vapor at 93°K. and in the solid-state spectrum at 93°K. were identical, and the alterations in absorbance, band width, and position of maxima were ascribed to molecular interactions. A series of aromatic hydrocarbons (21) at about 100°K. showed resolution of room-temperature bands into subpeaks; absorptions classified as α -, β -, and para-bands by studies of analogous series of molecules exhibited distinctive and characteristic differences in shifts of position at low temperatures (22). Studies on compounds of biological origin have included porphyrins (23, 24) and chlorophylls (25, 26), where resolution of bands was sufficient to enable the construction of tentative term diagrams; purines and pyrimidines (6, 27), where cryoabsorption effects are variable and may be dependent on the degree of hydration (5); cholesterol (28), which shows resolution of new bands in the infrared region; and amino acids (27) among which the aromatic acids show cryoabsorption changes. The spectra of proteins at low temperatures show changes due to their aromatic amino acid components (29, 30) or to prosthetic groups such as hemes (31) or carotenes (10). Amorphous polymeric molecules at 4°K. show very small spectral changes, although one band of a crystalline polymer polythene was sharply narrowed (32).

Intermolecular forces and the orientation of molecules in the solid state and in crystals have been studied by these methods. The internal electrical field strength of rare-earth salts at 53°K. was estimated at 10^6 volts per cm. by comparison of cryoabsorption spectra with those produced by external fields (33). Polarized infrared spectra of N-acetylglycine and diketopiperazine at 88°K. (34) and of ammonium nitrate, thallos nitrate, and plumbous nitrate at 113°K. (35) were correlated with X-ray data, and indicated coupling between molecular and lattice modes. Studies on two types of diamond at about 100°K. (36) permitted their differentiation on the basis of absorption in the ultraviolet region.

Cryoabsorption spectra have been used to demonstrate monomolecular chemical reactions. The rigidity of media vitreous at low temperatures was used by G. N. Lewis (37) to limit diffusion and to eliminate bimolecular reactions. A number of monomolecular reactions of complex organic molecules, involving photodissociation, photoionization, and photooxida-

tion, were observed at about 100°K. Free radicals were identified by their absorption spectra; kinetic studies were not reported. Enzyme reaction velocities, involving dissociation of an enzyme-substrate complex, have recently been measured at low temperatures (38).

Molecules and configurations unstable at ordinary temperatures have been identified by their cryoabsorption spectra in other studies. Spectrophotometric observations of the reactions of rhodopsin, the biological pigment intermediary in the translation of light to nervous impulses, were conducted in fluid media at 173–258°K. (39). The transformation of the photochemical reaction product, lumi-rhodopsin, into another unstable intermediary by a dark reaction on slight warming was shown. The kinetics of the reaction after illumination indicated a monomolecular process. The equilibria shift between isomers of chlorophylls in fluid media as temperature is increased from 75°K. to 300°K. (26). Refrigeration methods must be used for the observation of spectra of configurations unstable at ordinary temperatures. Irradiation of conductive alkali halogenide crystals at low temperatures displaces electrons from the lattice. The cryoabsorption spectra of the colored centers produced by electron displacement in NaCl—"F centers"—indicate that the frequency absorbed is accounted for by the ionization energy of sodium atoms (40).

The further extension of application of absorption spectroscopy by cryoabsorption techniques appears feasible in several directions. The most immediate problem is the improvement and standardization of refrigerated cells. Such developments should permit the investigation of quantitative cryoabsorption methods, which would offer increased sensitivity and resolution (specificity) over conventional room-temperature techniques. Another interesting extension of investigations is indicated in studies on the kinetics and intermediary compounds of catalytic processes in biological and nonbiological systems, where low temperatures limit diffusion and prolong the existence of unstable and transitory molecules. It is to be hoped that with the development of general interest in this relatively recent refertilization of absorption spectroscopy by low-temperature physics, many new approaches to old problems will be conceived.

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GRADUATE CHEMISTRY COURSE OFFERINGS IN AMERICAN COLLEGES AND UNIVERSITIES

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MOST chemistry departments awarding the Ph.D. degree face the continuing problem of reevaluating their graduate course offerings. In carrying out such a reevaluation it might prove helpful to know what graduate chemistry courses are now being offered by other American colleges and universities awarding the Ph.D. degree.

This analysis was based on data taken from graduate bulletins and some supplementary departmental pamphlets from 81 colleges. Each principal area covered (analytical, inorganic, organic, physical) was subdivided into from seven to 13 subareas, and the number of credits offered within each of these subareas was tabulated. The mechanics of delineating the subareas was, in many cases, somewhat arbitrary, and it was necessary to distribute some courses into more than one subarea.

All credits tabulated are semester credit hours. A quarter credit hour was considered to be equal to two-

thirds of a semester credit hour. Several special credit systems were converted according to the directions given in the graduate bulletin.

The resulting tabulations are given in Tables 1-4. The values in the "average credits" column were found by dividing the total tabulated credits in the subarea by 81. The values in the "maximum credits" column are the largest number of credits offered within the subarea by any one college.

The credit distribution of course offerings within each of the four principal areas considered is shown in Table 5.

Table 5 indicates the very wide range in course offerings in American colleges and universities. This in turn indicates very wide differences in opinion as to what constitutes a proper balance between formal course work, learning via other channels, and the inculcation of research methods and attitudes through participation in graduate research.

TABLE 1
Analytical Chemistry Graduate Course Offerings

	<i>Av. credits</i>	<i>Max. credits</i>
(1) Instrumental Analysis Electroanalysis, optical analysis, absorption spectrometry, emission spectroscopy, polarography, radioanalysis, X-ray diffraction analysis	4.0	14
(2) Analytical Theory	2.8	13
(3) Advanced Laboratory	2.0	8
(4) Microanalysis; Microscopy	1.7	12
(5) Special Analytical Procedures Gas analysis, rock analysis, rare-element analysis, water analysis, general technical analysis, metallurgical analysis, fluorine analysis, oil analysis, iron and steel analysis, food analysis	1.7	12
(6) Seminar; Recent Advances in Analytical Chemistry	0.5	6
(7) Unassigned Special Topics	0.2	6
Average total analytical credits	12.9	

TABLE 3
Organic Chemistry Graduate Course Offerings

	<i>Av. credits</i>	<i>Max. credits</i>
(1) Organic Theory Electronic interpretations, reaction mechanisms, structure determination, stereochemistry, free radicals, catalysis, organic acids and bases	4.7	13
(2) Organic Analysis, Qualitative and Quantitative	4.4	10
(3) Organic Reactions; Organic Syntheses	3.9	12
(4) Advanced Laboratory	3.0	9
(5) Natural Products Steroids, terpenes, carbocyclics, alicyclics, alkaloids	2.1	9
(6) Heterocyclics	1.4	4
(7) Unassigned Special Topics	1.3	12
(8) Polymers; Textiles; Plastics; Paints, Varnishes, Lacquers	1.1	12
(9) Organononmetallics Organophosphorus, organosilicon, organonitrogen, organosulfur, organofluorine	0.9	9
(10) Carbohydrates Sugars, starch, paper and wood	0.8	10.3
(11) Seminar; Recent Advances in Organic Chemistry	0.7	6
(12) Organometallics	0.2	3
(13) Miscellaneous Special Topics Dyes, petroleum chemistry, hydrocarbons, polycyclic hydrocarbons, organic reagents	0.2	3
Average total organic credits	24.8	

TABLE 2
Inorganic Chemistry Graduate Course Offerings

	<i>Av. credits</i>	<i>Max. credits</i>
(1) Inorganic Reactions; Periodic Relationships	2.7	12
(2) Inorganic Theory Atomic and molecular structure, bonding and valence, magnetochemistry, acid-base theory, crystal chemistry, inorganic catalysis	2.6	7
(3) Advanced Laboratory	1.6	7
(4) Less Familiar Elements	0.7	4
(5) Unassigned Special Topics	0.7	4
(6) Coordination Compounds	0.5	3
(7) Seminar; Recent Advances in Inorganic Chemistry	0.4	4
(8) Miscellaneous Special Topics Inorganic fluorine compounds, inorganic nitrogen compounds, inorganic silicon compounds, ammonia system of compounds, di-electrics	0.4	21
(9) Nonaqueous Solutions; Nonaqueous Solvents; Liquid Ammonia Solutions	0.3	3
Average total inorganic credits	9.9	

TABLE 4
Physical Chemistry Graduate Course Offerings

	<i>Av. credits</i>	<i>Max. credits</i>
(1) Atomic and Molecular Structure Spectroscopy, X-ray diffraction and crystal structure, electron diffraction, electron microscopy	5.1	16.7
(2) Theoretical Chemistry Statistical thermodynamics, statistical mechanics, quantum mechanics, kinetic theory of gases	5.0	16.7
(3) Thermodynamics (Except Statistical); Gaseous State (Except Statistical); Liquid State	4.9	11
(4) Surface Chemistry; Colloids; High Polymers; Chromatography; Ion Exchange	4.0	16
(5) Chemical Kinetics; Photochemistry; Catalysis; Free Radicals	3.6	10
(6) Electrochemistry; Solutions; Corrosion	2.3	9.5
(7) Nuclear Chemistry; Radioisotope Tracers	2.3	12
(8) Advanced Laboratory	1.5	6
(9) Physical Organic	1.4	6
(10) Phase Equilibria; Metals and Alloys	1.2	9
(11) Unassigned Special Topics	0.7	8.7
(12) Seminar; Recent Advances in Physical Chemistry	0.6	4
Average total physical chemistry credits	32.7	

TABLE 5
Credit Distribution Among Colleges

	<i>Anal.</i>	<i>Inorg.</i>	<i>Org.</i>	<i>Physical</i>	<i>Total</i>
Minimum	0	0	12	10	32
75% of colleges above	7	6	19.5	24	57
50% of colleges above	12	9	24.7	30	84
25% of colleges above	19	14	29.2	42	91.5
Maximum	44	39	58.0	67.3	164
Average total credits 80.2					

THIOACETAMIDE AS A SOURCE OF HYDROGEN SULFIDE IN QUALITATIVE ANALYSIS

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FOR a number of years a water solution of thioacetamide has been used as a source of hydrogen sulfide to precipitate metal sulfides in qualitative analysis.¹ The thioacetamide hydrolyzes in both acid and alkaline solution, especially at higher temperatures, yielding hydrogen sulfide.

There are important advantages in using this reagent instead of hydrogen sulfide:

(1) Toxicity and disagreeable odor of hydrogen sulfide are eliminated, as very little of the gas escapes.

(2) Thioacetamide does away with the use of generators and compressed-gas cylinders.

(3) There is homogeneous precipitation of the metal sulfides, which are easier to filter and centrifuge.

(4) The over-all time needed for the analysis of the copper-tin group (Group II) is shorter than with hydrogen sulfide, since arsenate is completely precipitated with the other metal sulfides and need not be sought in the centrifugate before analysis of the zinc group (Group III).²

However, there are disadvantages which have not been considered and which might outweigh the advantages:

(1) The effect of oxidants like nitric acid, arsenate, and ferric ions in destroying the thioacetamide, thus not giving complete precipitation of certain metal ions as sulfides—*i. e.*, cadmium, lead, and tin.

(2) The oxidation of thioacetamide to sulfate ion by these oxidants, resulting in the precipitation of lead, barium, strontium, and possibly calcium.

(3) The possibility of the precipitation of certain metal ions (zinc, nickel, cobalt, and iron) as sulfides in the copper-tin group (Group II), owing to the fact that the hydrolysis of thioacetamide yields acetate ion, which would form a buffered solution with a low hydrogen-ion concentration.

(4) The presence of thioacetamide in the centrifugate from precipitation of the copper-tin group (Group II) would prevent preliminary indications of the

trivalent metal ions (aluminum, chromium, and iron) by precipitation of their hydroxides.

Each of these disadvantages was experimentally investigated, and a method was worked out which successfully overcomes them. In the experimental work a saturated water solution (13 per cent) of the thioacetamide was used in order to have the smallest volume. It was found that one ml. was necessary to bring about complete precipitation of 25 mg. of the copper-tin group in the presence of 10 mg. of arsenic as arsenate (which also is completely precipitated), and 10 mg. of ferric ion. However, the hydrogen-ion concentration eventually must be reduced to 0.1 *N* in order to precipitate cadmium ion completely.

The method developed adjusts the acidity of the solution to 0.3 *N* hydrogen ion, starting with one ml. of the copper-tin group containing a maximum of 25 mg. of metal ions; first, any acid is neutralized with concentrated ammonia, then the solution is made just acid with dilute HCl, and two drops of concentrated HCl is added. The volume is usually two ml. at this point. The solution is put in a 20-ml. test tube and warmed in a boiling-water bath. Then the tube is closed with a one-hole rubber stopper in which a medicine dropper, having a plug of cotton about 1/4 inch long in the narrow part, is inserted so the narrow end extends slightly below the inner end of the rubber stopper. One ml. of water is put in the medicine dropper and the test tube is allowed to remain in the boiling-water bath for five minutes. This apparatus causes a slight internal pressure and some of the escaping hydrogen sulfide dissolves in the water in the medicine dropper. The cotton breaks up the hydrogen sulfide into small bubbles so that the water in the medicine dropper is not forced out. When the test tube is removed from the bath, the water in the medicine dropper runs into the test tube. Four ml. of water is added to the solution, the test tube is put back in the bath, and the special stopper is replaced, with one ml. of water in the medicine dropper. After five minutes the test tube is removed, allowing the water in the dropper to run in. The final concentration of the solution under these conditions is 0.1 *N* hydrogen ion.

Separately, 10 mg. of arsenate ion and 10 mg. of ferric ion gave a negligible amount of sulfate ion with one ml. of thioacetamide solution in 0.3 *N* hydrogen ion eventually reduced to 0.1 *N*. When concentrated nitric acid was used to destroy the thioacetamide in the centrifugate from precipitation of the copper-tin group,

¹ BARBER, H. H., AND E. GRZESKOWIAK, *Anal. Chem.*, **21**, 192 (1949); BARBER, H. H., AND T. I. TAYLOR, "Semimicro Qualitative Analysis," Revised ed., Harper and Bros., New York, 1953; SORUM, C. H., "Introduction to Semimicro Qualitative Analysis," 2nd ed., Prentice-Hall, Inc., New York, 1953; HOGNESS, T. R., AND W. C. JOHNSON, "Qualitative Analysis and Chemical Equilibrium," 4th ed., Henry Holt and Co., New York, 1954; FLASCHKA, H., *Chemist-Analyst*, **44**, 2 (1955).

² CURTMAN, L. J., "Introduction to Semimicro Qualitative Chemical Analysis," Revised ed., The Macmillan Company, New York, 1950, p. 270.

two mg. of sulfate ion, determined as barium sulfate, was found.

Using 10 mg., separately, of nickel, cobalt, zinc, and ferric ion in 0.3 *N* hydrogen-ion solution eventually reduced to 0.1 *N*, one ml. of thioacetamide, and following the above method, it was found that approximately 2.5 mg. of zinc ion was precipitated as the sulfide, but none of the others.

In order to obtain preliminary indications of the trivalent metal ions (Al^{+3} , Cr^{+3} , and Fe^{+3}) of the zinc group by precipitation of their hydroxides, it is necessary to destroy the thioacetamide left in the centrifugate from the copper-tin group. Nitric acid is objectionable since it causes sulfate ion to form. It was

found that adding one ml. of concentrated HCl and evaporating the solution to three ml. caused all the thioacetamide to be hydrolyzed and the hydrogen sulfide to be driven off, as shown by test with moist lead acetate paper. The same procedure was used to remove any thioacetamide in the centrifugate from the zinc group, before nitric acid was added.³

Thus, the only drawback in this method of using thioacetamide is the loss of about 25 per cent of the zinc ion in the copper-tin group. Following the procedures in a well known book² and substituting thioacetamide for hydrogen sulfide according to the method given above, over 200 students obtained excellent results.

³ *Ibid.*, p. 282.

● SIMULATED RESEARCH FOR FRESHMEN

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THE essence of physical science is a mode of procedure. A question is asked of nature in the form of an experiment, and the answer to the question is determined by an interpretation of the experimental results. Nothing could be more exciting to the student who has any potentialities as a scientist. The laboratory portion of our courses can and should use this excitement in motivating the student. It seldom does.

In many traditional laboratory assignments the student does not perform an experiment, but rather a personalized demonstration. Such activity has some merit in that it gives the student personal contact with the actual chemicals involved, but it is expensive in time and materials, is often inferior in efficiency to a well performed demonstration by the teacher, and may even degenerate into mere "busy work." Often the brighter and more independent student is disgusted by such an inane procedure and devises methods of circumventing what he regards as unreasonable demands. Sometimes he cheats, and except in the rare cases where he is caught, receives a higher grade for a dishonest report than for an honest one.

EVALUATION OF QUALITATIVE ANALYSIS

One successful modification of the older procedures is to introduce unknowns. Since the answer can no longer be determined by reading a textbook, the

student is not encouraged to cheat and is encouraged to make valid observations. Qualitative analysis traditionally introduces a host of unknowns. In many colleges and universities it has been absorbed into the elementary work and has almost disappeared from the curriculum as a separate course. In schools where this transition has occurred, the gain in student interest and morale in the elementary laboratory has usually been pronounced.

There is still room for improvement in traditional qualitative analysis. Laboratory note taking in the typical freshman qualitative analysis course tends to be very sketchy, and reports often consist merely of a list of symbols of the elements found. Mediocre students, slavishly following directions, are too often able to achieve satisfactory grades without ever doing any real thinking. At no point is the student forced to make a real choice as to what he should try next. The making of a correct choice as to the next step is not only a lot of fun for the potential chemist, but the ability to do so is probably the principal characteristic of persons who eventually become outstanding as research men. Our typical undergraduate teaching procedures kill rather than nurture this ability. The better and more carefully written the laboratory manual, the less likely is the student to exercise originality. In fact, the superior student who might some day be

an ornament to the chemical profession is likely to abandon it at this stage as a "cook book" subject.

THE SIMULATED RESEARCH PROJECT

At Northwestern University we have been conducting an educational experiment designed to correct some of these deficiencies. By substituting anion analysis for the usual descriptive nonmetal chemistry, and omitting desirable but unessential duplication of unknowns, we are able to use several weeks at the end of the school year for more fruitful and exciting activities on the part of the student. Each student actually undertakes a simulated research problem. He is given a copious sample of a solution of some ion that was not covered in the regular scheme, and is asked to identify the ion, adopt or devise a scheme of analysis for an unknown containing the usual scheme ions plus *this one* extra ion, and to analyze a couple of rather simple general unknowns which may or may not contain his personal ion.

The mechanics of administration are quite simple. As rapidly as the students complete the traditional assignment, they are turned loose with 25 ml. of a solution of an ion and the following directive.

RESEARCH PROBLEM

In the laboratory work thus far you have been given rather specific instructions as to procedure. You are now to be given an opportunity to use your initiative fully and to gather for yourself the facts which will enable you to plan and carry out an analysis.

You will be given a solution that contains an element not covered by the analytical scheme in our text. It may be any one of the following: Li, Cs, Au, Be, In, Tl, Th, V, Mo, W, U, Pt, Ce, Te. You are to "play" with this solution in the laboratory for about an afternoon, finding out all that you can about it.

One of the first things to do might be to find out where it would appear in the regular scheme. Does it form an insoluble hydroxide? Does it form soluble complex ions with NH_3 , CN^- , $\text{S}_2\text{O}_3^{2-}$, etc.? Is the hydroxide amphoteric? Is the ion a reducing or an oxidizing agent? Does it form an insoluble sulfate, oxalate, etc.? Does it give a flame test or a bead test? While you are doing this kind of experiment, keep copious notes.

When you have found out a considerable amount of information you will want to go to the library. In the reserve room you will find "A Comprehensive Treatise on Inorganic and Theoretical Chemistry" by J. W. Mellor. This 15-volume set of books describes the chemistry of the possible elements rather completely. Concerning each element there is a very helpful section entitled Reactions of Analytical Interest. Other small reference books which may prove useful are: Latimer and Hildebrand, "Reference Book of Inorganic Chemistry"; Hopkins, "Chemistry of the Less Familiar Elements"; McAlpine and Soule, "Qualitative Chemical Analysis."

By comparison of your laboratory results with the reaction behavior described in the reference books you may be able to identify your element, but you will probably wish to return to the laboratory to do a few critical experiments. Remember to take notes both in the laboratory and the library.

On the basis of your original experiments in the laboratory and others that have been suggested by library reading but verified in the laboratory, you should now be able to identify your element and to plan an analytical scheme for unknowns containing your "new" element in the presence of any or all of the elements in the regular scheme. Do so, and submit a voluminous report including a description of your laboratory experiments, a flow sheet of your new scheme that provides for your new element,

and a summary of any pertinent information that you have gleaned from the library. This report is due at the close of your last laboratory period preceding May 22.

In working out this research problem you are to feel perfectly free to consult other library sources, the members of the teaching staff, or your fellow research workers. Since the members of the staff will have access to information concerning the identity of your "new element" they will not make specific recommendations, but their ideas about general methods of attack may be helpful. Consult them freely, particularly when you have exhausted your own ideas as to possible modes of procedure. Remember, however, that you yourself have done the experimental work and that you have more direct information about your problem than anybody else.

The ultimate test of the validity of your work and your conclusions is to apply your scheme to the analysis of unknown solutions. You will be given two general unknowns, one or both of which may contain your new element. Analyze these according to your own new scheme and report the results.

The identification of your unknown element will probably take two weeks, leaving another two weeks for the analysis of the two unknown solutions.

You will be graded on initiative, originality, perseverance, independence, and the excellence of your report, as well as on the analysis of the unknowns.

It may happen that in your work you will need a reagent not on the side shelf. A list will be maintained on the bulletin board where you may record reagents that you desire. By the next laboratory period the reagent will either be on the side shelf, or it will be noted on the list that the reagent is unavailable.

STUDENT RESPONSE

The students went to work with enthusiasm and the instructor experienced one of the most thrilling episodes in his teaching career. Laboratory note taking was no longer a chore that an unreasonable teacher insisted upon, but a perfectly logical and necessary aid in arriving at an objective. Accurate laboratory observation was of vital interest to the individual student. Differences in reaction for different valence states became something very real. The privilege of extra time in the laboratory was demanded. Groups of students argued chemistry in the halls, in the laboratory, and in the lecture rooms before and after class. The librarian complained that the students disturbed others by their arguments in the library. The students dug up other (and, of course, much better) reference books. Several of the students who had acquired a reading knowledge of German in high school hunted up classical German treatises and found them extremely helpful. A few even consulted original journal articles and many were impressed with the real necessity of acquiring a reading knowledge of German at the earliest opportunity.

All of the students succeeded in identifying their ions, concocting or adapting an analytical scheme, and using the latter to analyze the general unknowns. Incidentally, the results were considerably better on these general unknowns than on those that just preceded the research project. These improved results were partly due to increased experience, but the writers like to think that they were in part due to better observation and better understanding of the nature of the chemical principles and reactions involved.

The final reports took various forms and were of

assorted excellence, but they were uniformly better than would be expected from experience in reading examinations and required written work from the same and similar students. The pride in personal accomplishment and the desire to present that accomplishment adequately stood out.

EVIDENCE OF RESEARCH PSYCHOLOGY

We have called the project "simulated research" and we believe that that term was fully justified by the results. (The students coined the name "super-duper unknown.") Most of the sensations of the active researcher were duplicated by the students. Several typical excerpts from the reports will illustrate this point.

[Student working on Ce⁺⁺] . . . I got this brown precipitate at least three times. The last time I added (NH₄)₂S, I added it far to excess and got a black sulfide. At this point I was sure I had vanadium. . . . When I started to confirm vanadium, I was in for quite a surprise. [Six tests that were negative for vanadium follow.] . . . Having eliminated vanadium rather decisively, I started again on the idea that it might be cerium. [Three positive tests for Ce⁺⁺ follow.] . . . Now that it began to look very much like Ce⁺⁺, I decided to do the test again which originally made me decide against cerium.

[Student working on uranium] . . . By comparison of these tests and my preliminary experiments, I suspected that my unknown element was uranium, and ruled out the other possibilities by the following reasoning. [Here the student recited the results of miscellaneous tests that he had performed in characterizing the ion.] . . . At this point further study on uranium was useless until I confirmed my suspicion by running several more tests for that element.

[Student working on platinum] . . . At this point I thought that I had gold. I added NH₄OH and HCl in an attempt to adjust the acidity for H₂S precipitation and noticed to my surprise that a yellow precipitate formed. I wondered about this precipitate for a while and then promptly forgot the whole thing. Later, while reading about some reactions of platinum, I found that NH₄Cl will form a yellow precipitate with H₂PtCl₆. . . . I was then convinced that my unknown was platinum.

[Student working on Tl⁺] . . . My next move was to run a series of tests to prove thallium and to disprove the other ions. I ran a flame test on my unknown which gave a green flame for a very short period of time. Thallium is the only ion which gives insoluble chlorides and also gives a green flame. I was now fairly sure that my unknown contained thallium. . . . As further proof of the presence of thallium, I tested the solubility of some of the precipitates. The chloride was soluble in hot water and the chromate was soluble in both nitric and sulfuric acids. . . . With AgNO₃ I should have obtained a white precipitate of TlNO₃·AgNO₃, but did not. . . . The number of positive tests for thallium that I got seemed to outweigh the number of tests that failed. I assumed that some did not work because of adverse conditions, such as concentration or temperature.

[Student working on Ce⁺⁺] . . . I became aware of the presence of cerium as my unknown through the interjections of several of my lab associates. Prior to their assistance, I had been laboring under the misapprehension that I was working with uranium. . . . Upon considering the possibilities of cerium, I saw that it was definitely indicated by my previous lab work.

Can any active research man read the above excerpts without recalling similar experience and sensations in his day-to-day work? You could talk to these students about a "tentative working hypothesis" and they

knew what you were talking about. They understood "the scientific method" because they had used it personally.

CONCLUSION

The chemistry teacher who habitually gives the traditional course will object vigorously to the time devoted to such projects. He will say that he has no time now for a great many important subjects that are susceptible to laboratory treatment and that if another 25 hours are subtracted -? *****. There is altogether too much validity in such objections for comfort. However, a sense of proportion is necessary. At best, about ten per cent of the facts and principles contained in the average course can be illustrated in the laboratory. Projects like this one will reduce the coverage to about eight and one-half per cent. The loss is one and one-half per cent of the total course content. This is a small price to pay for the enthusiasm generated, and for the very real understanding of the specific nature of the qualitative scheme and of the general nature of scientific procedure. Best of all, the students are given some small indication of the excitement of experiment.

ACKNOWLEDGMENT

We desire to thank Dean S. E. LeLand of the College of Liberal Arts for furnishing funds to pay for additional laboratory assistance during the early experimental phases of this project.

1	A	2	C	3	I	4	D	5	P	6	P	7	M	8	E	9	C	10	R	11	U			
12	R	13	A	14	R	15	E	16	A	17	H	18	A	19	S	20	H	21	E	22	M			
23	E	24	L	25	E	26	C	27	T	28	R	29	O	30	M	31	O	32	T	33	I	34	V	E
35	A	36	N	37	A	38	T	39	A	40	S	41	E	42										
43	D	44	A	45	U	46	N	47	T	48	O	49	E	50	R	51	B	52	I	53	A			
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64	R	65	O	66	C	67	E	68	T	69	H	70	E	71	R	72	Y	73	E	74	S			
75	A	76	V	77	E	78	R	79	S	80	E	81	L	82	A	83	L	84	A	85	E			
86	C	87	E	88	R	89	I	90	C	91	M	92	G	93	U	94	E	95	S	96	S			
97	C	98	A	99	T	100	I	101	O	102	N	103	S											
104	T	105	H	106	E	107	R	108	M	109	O	110	C	111	O	112	U	113	114	115	116	117	118	119
120	V	121	E	122	R	123	A	124	R	125	A	126	Z	127	E	128	A	129	130	131	132	133	134	135
136	A	137	L	138	E	139	A	140	L	141	E	142	X	143	R	144	A	145	146	147	148	149	150	151

Solution to Crossword Puzzle on Page 448

LECTURE-TABLE THERMOMETER AND VOLTMETER

FREDERIC B. DUTTON

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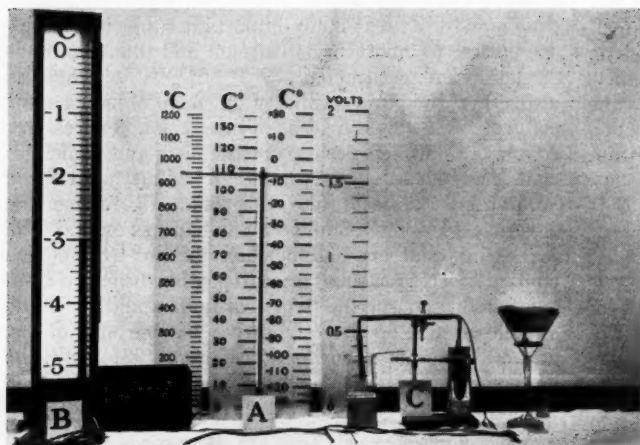


Figure 1. Lecture-table Thermometer

Foreground, thermocouples; C, ten-junction thermocouple mounted for freezing-point-lowering measurements; A, alternate scales; B, extension cord for thermocouple or cell connections; extreme right, funnel for separating ice from solutions.

LECTURE demonstrations involving temperature changes present a problem because the usual method of observing temperature is the ordinary thermometer, a device that can be observed by only one person at a time. This difficulty has been met by calling upon a student from the class to read the thermometer, or avoided by omitting such demonstrations from the program.

A sensitive temperature-indicating device that has a reasonably rapid response and would be visible to a large group would greatly increase the scope of phenomena that can be demonstrated to classes. To meet this requirement it was decided to build a thermometer that would indicate readings on a scale in front of a four-foot fluorescent lamp.

Thermocouples, resistance thermometers, and thermistors are all available as sensing elements used in conjunction with suitable potentiometers or bridge circuits for translating electromotive force or resistance into temperature readings. The thermocouple was selected for the present application because of its ease of construction, and economy. Since its output is measured with a potentiometer, the same circuit may be used to determine the electromotive force of electrochemical cells. One basic instrument can be used as both thermometer and voltmeter simultaneously.

Information on the theory and construction of thermocouples is available from many sources. A useful

pamphlet entitled "Thermoelectric Thermometry" has recently become available.¹

The lecture-table thermometer consists of a thermocouple, a potentiometer, a converter-amplifier, a motor and gear train, an indicator, and lamp and scale, shown in Figures 1, 2, and 3.

CIRCUIT

The circuits are shown schematically in Figure 4. A three-volt battery is connected across the end of the 1000-ohm potentiometer R1 through switch S1. The moving potentiometer contact makes it possible to feed from 0 to 3 volts to the balance of the circuit. This voltage is measured by the voltmeter V. Two volts is the usual operating potential.

One side of the battery circuit is connected to the moving contact of a five-position switch S3.

¹ DIKE, PAUL H., "Thermoelectric Thermometry," available at \$1 from The Leeds and Northrup Co., Philadelphia, Pa.

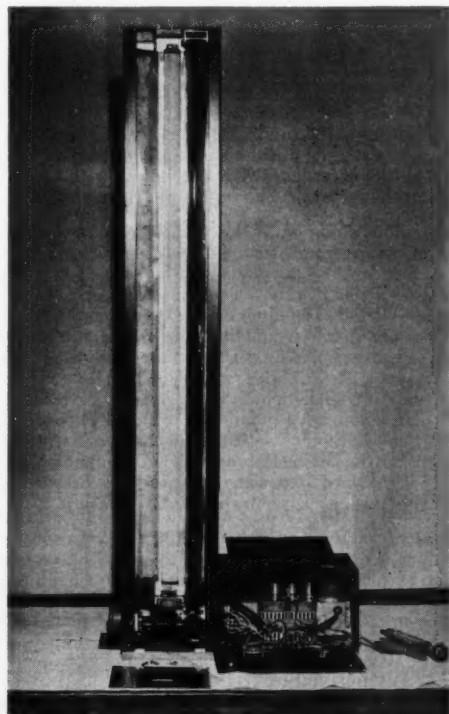


Figure 2. Thermometer with Scale and Front Panels Removed

This makes it possible to place 0, 39,000 ($R3$), 399,000 ($R3 + R4$), or 799,000 ($R3 + R4 + R5$) ohms in series with the 1000-ohm Helipot $R2$, and fixes the voltage drop across $R2$ at 2, 0.05, 0.005, 0.0025 volts, respectively. (The fifth position on the switch $S3$ is not used on this model.) The selected value then represents full scale deflection of the indicator. By varying the position of the moving contact of the Helipot $R2$, any desired fraction of this voltage is fed into the amplifier in opposition to that furnished by the thermocouple Tc . The two, double-pole, double-throw reversing switches $S4$ and $S5$ make it possible to establish the zero point at the top or bottom of the scale.

The converter amplifier is a Brown "Elektronik" continuous-balance unit and the servo-motor designed to be used with it was obtained from the same source.²

When the potential difference between terminals Tx and Tz differs by more than a fraction of a microvolt, the output of the amplifier drives the servo-motor in a direction depending upon whether the thermocouple or the potentiometer is furnishing the higher potential. Connections from these terminals lead through the reversing switch $S5$ to one side of the thermocouple and through the resistor system to the battery. The other side of the thermocouple connects directly to the battery.

The shaft of the servo-motor is connected by gears to the rotor of the Helipot and to a sprocket that drives a film between the lamp and the scale. Thus, the system is self-balancing and indicates the balance point on the scale which may be calibrated in any appropriate units.

CONSTRUCTION

Five scales have been made for this instrument. These are +20 to -130°C. for measuring the temperature of "dry ice," the freezing point of mercury, etc., 0 to -5°C. for freezing-point-lowering measurements, 0 to 130°C., 0 to 1200°C., and 0 to 2 volts. This last scale is used for the measurement of the voltage of electrochemical cells.

With the +20 to -100°C. range a copper-constantan thermocouple is used. For the 0 to -5°C. range a ten-junction chromel-constantan couple was constructed, since this metal combination gives the largest response per degree of temperature change. For the higher temperatures a chromel-alumel couple is used. Many other combinations are, of course, possible. To avoid the necessity for fixed junction compensation we use an ice bath for the reference junction with all but the +20 to -100°C. scale. For the latter, water at 20°C. is used as a reference.

The indicator is a strip of 35-mm. photographic film, half of which has been exposed and developed, the other half remaining clear.

² Purchased from the Minneapolis-Honeywell Regulator Co., continuous balance unit part No. 353170-18, motor part No. 76750, 27 r. p. m.

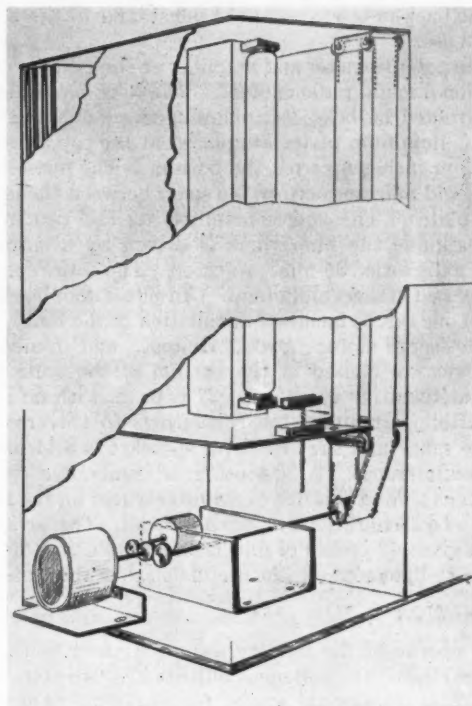


Figure 3. Schematic Section Showing Some Details of Mechanical Construction

The edge of the black area marks the point on the scale corresponding to the value being measured. The film forms a continuous loop that passes over spools at the top and a spool and sprocket at the bottom of the scale housing. The scale inscriptions are painted on the back side of a Plexiglas sheet 1/8 in. x 6 1/2 in. x 4 ft., which has been scoured with wet sandpaper to make it translucent. The scale slides in slots at the front of the supporting column, and additional slots are provided

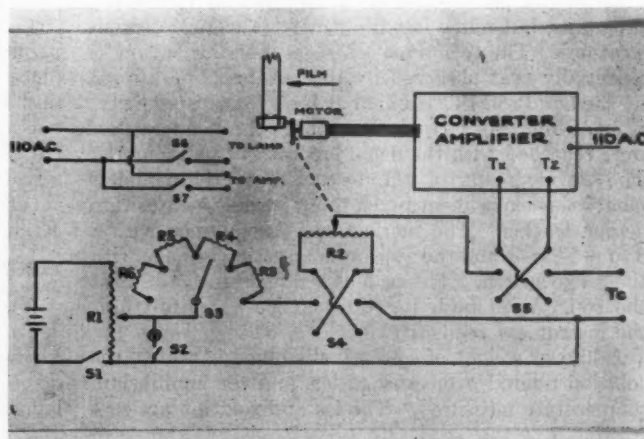


Figure 4. Electrical Circuits

at the back of the housing for the storage of the scales not in use.

The potentiometer and amplifier are housed in a conventional metal radio cabinet. The scale box frame is constructed of 1- × 2-in. aluminum channel. Three 1/4-in. aluminum plates are placed at the top, bottom, and four inches up from the bottom. The fluorescent lamp and reflector occupy the space between the upper two plates. The spools mounted on the two upper plates guide the film which is driven by a sprocket from a discarded 35-mm. projector. The entire column is enclosed in sheet aluminum. An access door has been cut in one side to facilitate installation of the film.

The servo-motor, gears, Helipot, and film-drive sprocket are housed in the bottom of the scale box. The motor drive operates at 27 r. p. m. with no load. The Helipot requires ten revolutions to traverse the entire range and the film-drive sprocket is 3.14 inches in circumference. A 20-tooth gear is mounted on the motor shaft and this drives a 40-tooth gear on the Helipot and a 28-tooth gear on the film spool. This arrangement gives 42 inches of film travel for ten revolutions of the Helipot contact, the useful length of the scale.

OPERATION

In operation the battery switch *S1* and voltmeter *S2* are closed; the voltage is adjusted to two volts with *R1*. The appropriate source, thermocouple or electrochemical cell, is plugged in with banana jacks and the range switch *S3* set at the appropriate position. The scale is illuminated by closing the lamp switch *S6* and the amplifier is turned on with *S7*. If zero is to be at the top of the scale switches, *S4* and *S5* are placed in the "up" position or in the "down" position for zero at the bottom of the scale. The zero point may be adjusted by raising or lowering the scale by means of the knurled knob at the bottom. The instrument is now ready for use.

USES

Freezing-point Lowering. Freezing-point lowering experiments have often been included in laboratory programs, but much less frequently as lecture demonstrations. The technique which is described below is essentially that observed by the author as performed by the late Professor Rumold at Kent State University, Kent, Ohio. As carried out by him, the temperatures were recorded with the usual laboratory thermometer. The development of the lecture-table thermometer makes this experiment much more feasible as a lecture demonstration. The thermometer is equipped with a 0 to -5° scale and the appropriate setting is made with the range switch. The scale is arranged so that 0 is at the top. With both junctions in ice-water mixtures the instrument reads 0°C.

A known weight of solute is dissolved in water, the solution poured over crushed ice, and the equilibrium temperature measured. The ice and solution are sep-

arated rapidly by pouring through a large funnel fitted with a screen. The solution is weighed, and we have the following data for an example using 30 g. of urea as solute.

Weight of beaker plus solution	830 g.
Weight of beaker plus solute	270 g.
Weight of water	560 g.
Weight of solute	30 g.
Molecular weight of solute	60
Freezing point of solution	-1.63

$$\frac{30 \text{ g. solute} \times 1000 \text{ g. water}}{560 \text{ g. water}} = 53.5 \text{ g. solute}/1000 \text{ g. water}$$

$$\frac{53.5 \text{ g. solute}}{60 \text{ (mol. wt.)}} = 0.89 \text{ molal}$$

$$\frac{1.63}{0.89} = 1.8 \text{ molal freezing-point constant}$$

Determinations of this sort neglect many of the refinements required for precision measurements, but these are sacrificed in order to obtain reasonable speed for a lecture demonstration. Determinations made in this manner can usually be completed in less than five minutes and give values ranging from 1.7 to 1.9. The experiment may then be repeated with different quantities of the same solute or with other solutes. We usually determine the constant using one solute and then use the constant thus obtained to calculate the molecular weight of a second "unknown" solute.

Temperature Measurements. The temperature of any object may be measured if an appropriate thermocouple and range setting are used. As an example the 20 to -130° scale is put in place, the range switch set at position number 3, and a single-junction copper-constantan thermocouple is connected to the instrument. With the reference junction held at 20°C. and the other junction held between pieces of dry ice the thermometer indicates a temperature of about -78°C.

With the single-junction chromel-alumel thermocouple, the range switch set at position 2, and using the 0 to 1200°C. scale, the temperature differences in various portions of the Bunsen-burner flame are readily demonstrated.

Voltage Measurements. The 0 to 2 volt scale is put in place. Leads with battery clips are connected in place of the thermocouple and the range switch set at position 1. When the clips are fastened to the terminals of a Daniel cell the meter will indicate 1.1 volts. Other cells may be used to demonstrate the e. m. f. series.

Other Uses. It is anticipated that this instrument can be adapted to pH and gas-pressure measurements.

ACKNOWLEDGMENT

Acknowledgment is gratefully made to Dr. R. J. Jeffries of the electrical engineering department of Michigan State College for suggestions which made the device practical, and to Dr. H. B. Thompson of this laboratory for advice freely given.

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TECHNICAL EDUCATION IN THE U.S.S.R.¹

SONYA G. MACHELSON

Library of Congress, Washington, D. C.

IT WAS the fashion, not so long ago, to claim that we did not receive any scientific literature from the Soviet Union, and if we did, it would not be worth the paper it was published on. But now, when Russia confronts us with jet aircraft, automation factories, and an atomic power station, our scientists and nonscientists alike are interested in Soviet science and Soviet scientific manpower. Many interested groups are conducting studies on education in the U.S.S.R.

According to statistics, in 1897 only 24 per cent of all persons in Russia above the age of nine could read or write. Forty nationalities did not have their own alphabet. In 1919 a decree was issued calling for elimination of illiteracy. Soon many schools for illiterates sprang up throughout the country, and in 1939 literacy increased to 90 per cent. The right of every citizen to an education is stated in Article 121 of the Constitution of the U.S.S.R. as follows:

Citizens of the U.S.S.R. have the right to education. This right is guaranteed by universal, compulsory elementary education; by free seven-year education; by a system of state scholarships to outstanding students in higher schools; by conducting instruction in the schools in the native language; by the organization in factories, state farms, machine-tractor stations, and collective farms of free vocational, technical, and agronomical training for the workers.

In 1930 universal and compulsory schooling of all children above eight was introduced. Four-year education was made obligatory throughout the country, and seven-year education in the cities and industrial areas.

In 1949 universal and compulsory seven-year education was extended to include rural areas as well. The current Five-year Plan calls for universal ten-year education in larger cities by the end of 1955, and in rural areas by 1960.

PRIMARY AND SECONDARY EDUCATION

General education is offered at three levels: primary (four-year study), incomplete secondary (seven years), and complete secondary (ten years). In principle, general education is conducted in the language native to the students. Any graduate of a national secondary school encounters some difficulty when he enters a university or institute, because most higher education is conducted in Russian. However, there are faculties in certain universities and some institutes, particularly pedagogical ones, where all teaching is in the local tongue. In 1938 Russian was made a required subject in all non-Russian schools.

Specialized education may begin on the secondary level in specialized schools, which are known as *tekhnikums*, and continue through the higher educational institutions, all of which, including universities, offer only specialized training programs.

The formal educational schools are paralleled by public educational institutions which make the program of the primary and secondary schools available through night and correspondence schools to persons unable to attend regular schools. On-the-job training, public lectures, clubs, and study groups also offer both technical and general training outside the regular school system.

The entire school system of the U.S.S.R. is regarded by Soviet educators as "polytechnical," because all students "are made familiar with the basic elements of the labor process. Studies of the sciences, for example, are coordinated with the study of their application in local industries in towns, or in the collective and state farm experimental station and the local machine and tractor station in the countryside."

A very significant development in recent years in the sphere of technical training was the organization of the Chief Administration of Labor Reserves under the Council of People's Commissars (October, 1940). The system was expected to provide industry with from 800,000 to 1,000,000 skilled workers annually. The pupils are given a general education in addition to being taught a craft or trade.

The *Labor Reserve Schools* are of two types: (1) Two-year trade schools which train metal workers, miners, workers for the chemical and petroleum industries, sea and river transportation, and communications. Boys from 14 to 17 and girls from 15 to 16 who have had at least four years of education are admitted. (2) Six-month factory-plant training schools to train semi-skilled workers, chiefly for coal and ore mining, metal working, petroleum production, and construction projects. Boys from 16 to 19 and girls from 16 to 18 are admitted, without regard to educational preparation. There is no tuition, and students are supported by the government during their schooling. All graduates of Labor Reserve Schools are required to serve four consecutive years at jobs and locations assigned by the Ministry of Labor Reserves. In the years from 1940 to 1945, from 500,000 to 600,000 were graduated annually from all types of Labor Reserve School.

Specialized secondary schools—*tekhnikums*—cover a wide variety of specialties: they prepare nurses, automobile mechanics, electricians, librarians, accountants, etc. The course of study varies from three to five years depending on the specialty. Students of both sexes,

¹ Presented at the 127th Meeting of the American Chemical Society, Cincinnati, March, 1955.

from 14 to 30, who have completed a seven-year school and who successfully pass entrance examinations in mathematics, Russian language and literature, and the Soviet Constitution are admitted. The *tekhnikum*s also cover the program of grades 7 to 10 of the ten-year school. Although most *tekhnikum*s offer scholarships to all students, a large number give them only to students who pass the entrance examinations with a mark "good" or "outstanding." Many *tekhnikum*s have correspondence schools and evening classes to which students of all ages are admitted, but only if they are currently employed at a job closely related to the specialty they have chosen to study. All *tekhnikum*s require payment of tuition of from 150 to 200 rubles per year (correspondence schools cost half as much). The graduates must spend three years working in the specialty in which they have been trained. According to an order of the Ministry of Higher Education, on February 20, 1952, students graduating from *tekhnikum*s with an outstanding rating may be admitted to higher educational institutions without entrance examinations and without having worked the three years required by law. In 1951-52 there were 1,384,000 students studying in 3543 *tekhnikum*s.

HIGHER EDUCATION

Higher education in all fields is provided by universities, institutes, academies, and other higher educational institutions. They are open to all persons from 17 to 35 who have finished secondary school. They must take entrance examinations in Russian language and literature and in other subjects related to the specialty they have chosen to study. Secondary-school graduates with gold or silver medals and *tekhnikum* graduates with outstanding marks may enter without entrance examinations.

Students who have "outstanding" or "good" marks receive scholarships from 140 to 315 rubles monthly, depending on the type of school and the number of years completed. About 80 per cent of the students receive scholarships. Some institutions provide living accommodations to all students, some only to out-of-town students; some schools offer three meals a day, some two, some none.

The Soviet Union claims to have about 900 such institutions, of which 33 are state universities, 19 polytechnical institutes, 20 correspondence schools, and the others, institutes devoted to a single branch of knowledge. Prior to 1914 Russia had 91 higher educational institutions with 112,000 students.

The academic year starts on September 1, and is divided into two terms with two weeks vacation in winter and two months in summer. Examinations are taken at the end of each term. The courses last from four to six years. To complete the course the student must defend a thesis or work project in addition to passing state examinations in order to qualify for the diploma which describes the work performed. No formal degree is conferred. Upon completion of the course the student is required by law to work for at

least three years at his specialty in a position and location designated by the government. In 1951-52 1,356,000 students were enrolled in 887 institutions.

Students wishing to complete a higher education without giving up their jobs may enroll in the correspondence schools or night schools established in some 450 of the universities or institutes, or in one of the 20 institutions devoted entirely to education by correspondence. In recent years 30 per cent of all graduates have been correspondence- or night-school students. The students are required to appear at the university twice a year to attend review lectures and do laboratory work; this is followed by examinations. They receive full pay during these periods. Graduates of correspondence schools take the same state examinations as the full-time students and on graduation enjoy exactly the same rights.

The only general subjects required of a science student are courses in Marxism-Leninism, economics, dialectical materialism—taking up about six to eight per cent of his classroom time—and a foreign language. His time is divided between general science courses (25-30 per cent) and the sciences of his specialty (62-70 per cent).

The Soviet government has made a great effort to increase enrollment in higher educational institutions in the postwar years. By 1954 the number of students advanced to more than 1,500,000. Widespread opportunities are provided for what we call postgraduate studies and scientific research as a career.

POSTGRADUATE WORK

Postgraduate students are of two types: the *Aspirant* studying for the degree of *Kandidat of Sciences*, and the *Kandidat* studying for the degree of *Doctor of Sciences*. These degrees are only roughly equivalent to advanced degrees of American universities; they require more postgraduate hours. Advanced degrees are conferred by certain universities and institutes as well as by some scientific research institutions attached to various ministries and other governmental agencies or to the Academy of Sciences and its branches. As of June, 1952, 278 such institutions had been authorized to confer both degrees, and an additional 192 to confer the *Kandidat* degree. The applicants must have a complete higher education, must not be over 40, and must show evidence of pedagogical or scientific research ability.

The *Aspirant* studies for three years. He has an advisor, a full professor or a Doctor of Sciences. His plan of study must be approved by the head of the institution. In addition to his specialized studies, he must study an additional foreign language. Upon finishing his studies he takes an examination and submits a thesis. He pays no fees and receives a scholarship amounting to 700 to 800 rubles a month. He is paid for 13 months a year, the extra month being for purchase of books, etc. He is entitled to two months of vacation.

A candidate for the *Doctor of Sciences* degree receives

a scholarship of 1300 rubles per month. A person who has made an outstanding contribution to science may receive a doctor's degree without defense of his dissertation. On completion of their academic work, *Kandidats* and doctors are directed to a place of employment by the governmental agency in whose institution they studied. According to Soviet claims, 484 Doctor of Sciences degrees were conferred in 1950-51; 27,000 graduates enrolled in 1952-53.

Fees. Nominal fees are charged by Soviet higher educational institutions. In Moscow, Leningrad, and capitals of the Union Republics the fees amount to 400 rubles a year. Elsewhere they amount to 300 rubles a year. Many students are exempt from payment: war veterans, disabled persons, orphans, children of soldiers, teachers, and doctors, and all students from the Asian and Central Asian Republics. The fees bear no relationship to the cost of education received; a student may receive in scholarships alone from 3000 to 7000 rubles per year.

Administration. Higher educational institutions are under the direct control and supervision of the Main Administration of Higher Educational Institutions of the Ministry of Culture. The remainder, although under the supervision of the Ministry of Culture as far as general policy is concerned, are under the control of other ministries (such as the Ministries of Transport, Agriculture and Procurement, or Health), or of Republic Ministries.

Publications. The greater part of Soviet scientific and technical books are published by a few large publishing houses, the most important of which is the Academy of Sciences of the U.S.S.R. In 1949 it published 295 titles or about 2,000,000 books. Since then the activity of this publishing house has increased markedly.

Specialized publishing houses such as Medgiz (Medical Publishing House), Gostekhizdat (State Technical Publishing House), Sel'khozgiz (State Agricultural Publishing House), etc., also publish a great amount of scientific and technical literature.

During 1918-27 only 5,400,000 copies were published; in 1928-37, 78,000,000 copies; in 1938-47, 95,000,000 copies. Including periodicals and smaller printed matter, the total output of scientific and technical literature during the years 1946-50 amounted to 32,700 titles or 306,000,000 pieces. The total number published in mathematics and natural sciences was 6700 titles or 79,000,000 pieces. The works of famous scholars have reached very large editions. Since 1918 the works of Mendeleev have appeared in 216,000 sets; those of Darwin in 350,000 sets.

Although book production is steadily increasing, it still does not satisfy all the demands. A year or two after publication almost all scientific books have been distributed. It has also happened that the sub-

scriptions for a particular book exceeded the number to be published even before the book came off the press.

The following statistics may be of interest.

In 1954, the Library of Congress received 3838 issues of Soviet periodicals and 4611 monographs, of which half were in science and technology. A spot check showed that the Library of Congress received the following monographs in the period from December, 1953, to March, 1954:

	U. S.	U.S.S.R.	Other countries
Science	370	229	367
Technology	478	890	401

In 1928-29 the student body numbered about 177,000; by the beginning of the second Five-year Plan, in 1933-34, this figure had increased to 504,000; by the beginning of the third Five-year Plan, in 1937-38, it had risen to about 603,000. And just before World War II, in 1941, there were about 800 universities and other higher educational institutions in the U.S.S.R. with about 667,000 students.

Simultaneously with the introduction of planning, decentralization and clarification of functions of various higher educational institutions took place. Prior to the revolution higher educational institutions were located in 16 cities, and now in 266 cities.

Problems of theoretical science are concentrated in the Academies and in some specialized research institutes. The universities are dedicated primarily to training research scientists and teachers; they also engage in research, theoretical and applied. The technical solution of problems concerning the development of the national economy is carried out in specialized institutes and in plant laboratories. The Soviet Union is said to spend one-eighth of its budget, nominally 15 billion dollars a year for education. This goes into student scholarships, teachers' pay, and new buildings. Fifty-thousand engineers are expected to be graduated in 1955, compared with 17,000 in the U. S.

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A NEW VAPOR-PRESSURE APPARATUS

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THE apparatus to be described was developed to simplify vapor-pressure studies in undergraduate laboratories. Data for pressure-temperature plots for liquids, solids, mixtures, and solutions may be obtained easily and rapidly.

The apparatus (Figure 1) consists of a long manom-

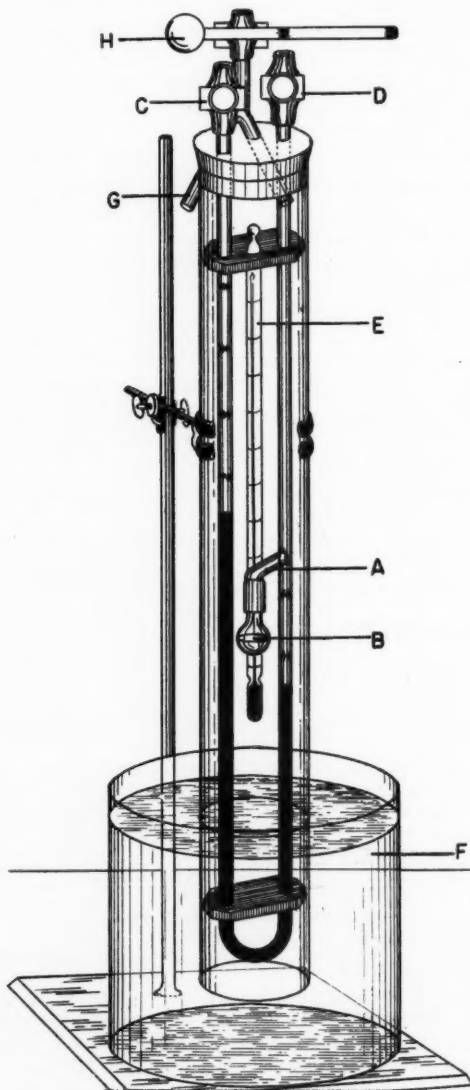


Figure 1

eter with a side arm *A* supported inside a large Pyrex tube. Both manometer arms are graduated in millimeters and equipped with airtight clamps or stopcocks at the top. The sample bulb *B* is a thin-walled bulb blown in 6-mm. tubing; in it is placed from two to three grams of the substance to be studied. The bulb and sample are connected tightly to the side arm by a short piece of Tygon plastic tubing.

The arm opposite the bulb is evacuated with a vacuum pump and closed tightly at *C*. With the sample bulb in place, the manometer arm supporting it is evacuated until the mercury levels are the same.

This arm is then sealed at *D*. At equilibrium the difference in heights of the mercury columns represents the vapor pressure of the sample at the temperature indicated by the total immersion thermometer *E*. To vary the temperature, water from the temperature bath *F* is forced into the large outer jacket. An aspirator connected to the exposed end of the Y-tube *G* provides sufficient vacuum to fill the outer jacket. By control of the flow rate through the aspirator, the water level in the large tube can easily be made to remain near the top.

As soon as the mercury columns come to rest, their heights and the temperature are recorded. The large tube is drained by shutting off the aspirator and opening clamp *H*. The bath temperature is increased 5–10°C., and water is again drawn into the outer tube to obtain the vapor pressure at this new temperature. By repetition of this process, curves similar to that shown in Figure 2 are quickly obtained. After all

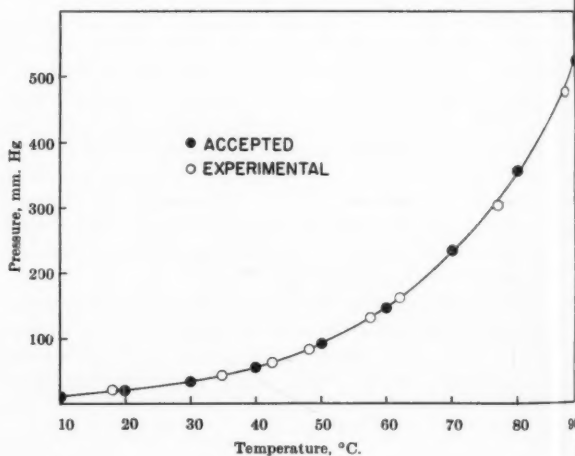


Figure 2

readings have been taken, bulb *B* is replaced with an empty bulb and the outer tube is filled with hot water. The vapors of the sample are then pumped out of the apparatus, which is now ready for the next sample.

The working model built by the authors was constructed from 6-mm. Pyrex tubing and gave pressure

readings up to 100 cm. It has been successfully used by a group of undergraduate physical chemistry students. Their results were in excellent agreement with values taken from the literature. The experimental and accepted plots obtained for water (Figure 2) are typical.

MONOCHLORAMINE

ERVIN COLTON

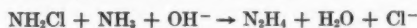
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MARK M. JONES

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EARLY in this century Raschig (1) found that when dilute solutions containing equimolar amounts of ammonia and sodium hypochlorite are mixed, the resulting solution does not give the characteristic reactions of the hypochlorite ion as would be expected if ammonium hypochlorite were formed. He also noted that the evolution of nitrogen, from the oxidation of the ammonia, is very slow. On the basis of these observations Raschig postulated the presence of monochloramine, NH_2Cl , in these solutions, and showed subsequently by analysis that the active oxidizing agent contains nitrogen and chlorine in the ratio of 1/1. Although he never succeeded in isolating pure monochloramine, Raschig studied many of the reactions of this elusive substance using aqueous solutions prepared from ammonia and sodium hypochlorite.

In subsequent investigations Raschig discovered that monochloramine can react with ammonia in basic solutions to form hydrazine in accordance with the equation:



Hydrazine is now prepared commercially by a process which essentially embodies the original observations of Raschig—a process usually called the Raschig synthesis.

Because much attention recently has been focused on hydrazine as a specialty fuel, monochloramine, the key intermediate in the Raschig synthesis of hydrazine, assumes an important role commercially. Furthermore, the bactericidal properties of monochloramine make this ammonia derivative one of the most widely used chemicals in the purification of water. For these reasons it seems appropriate to summarize certain aspects of the chemistry of monochloramine.

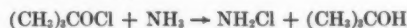
PREPARATION

Monochloramine is formed, as was shown by Raschig, through the interaction of ammonia and inorganic hypochlorites in accordance with the equation:

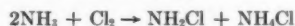


This method of synthesis is still the most convenient for the preparation of aqueous solutions of monochloramine (2). Other reactions in which monochloramine is formed include the following:

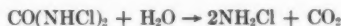
(a) The reaction between tertiary butyl hypochlorite and ammonia (3):



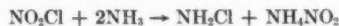
(b) The reaction between chlorine and ammonia, either dissolved in water (4, 5) or in the gaseous state with nitrogen as a diluent (6, 7):



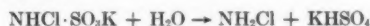
(c) The hydrolysis of dichlorourea (8):



(d) The reaction of nitryl chloride and ammonia at -75°C ., in which monochloramine is reported to be one of the products (9):



(e) The acid hydrolysis of potassium chloraminosulfonate (10):



Reactions (a), (b), and (c) have been used to prepare monochloramine as an intermediate for the preparation of hydrazine. Reactions (d) and (e) are of academic interest. Because of the instability of monochloramine, it is generally employed in aqueous solution or in other suitable nonaqueous solvents such as diethyl ether.

PROPERTIES

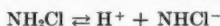
Monochloramine has been isolated only once (11) by passing the vapors of an aqueous solution over potassium carbonate and condensing the product at liquid-air temperature. The pure substance forms colorless

crystals melting at -66°C . and decomposing at slightly higher temperatures. Monochloramine is soluble in water and in diethyl ether, the distribution ratio between the two solvents being approximately one (11). Qualitative studies on the extractability of monochloramine from aqueous solutions with various nonaqueous solvents show the following order of decreasing effectiveness (12):

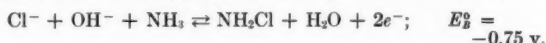
diethyl ether > isopropyl ether > β,β' -dichlorodiethyl ether > benzyl ether > *sym.*-tetrachloroethane > butyl ether > chloroform > benzene > chlorobenzene > carbon disulfide > carbon tetrachloride > low-boiling petroleum ether > cyclohexane

Monochloramine is highly useful in water treatment as a means of destroying pathogenic bacteria. Ingols and co-workers (13) have shown recently that, in comparison with hypochlorous acid, monochloramine requires much more time and larger concentrations of oxidation capacity to bring bacterial death.

Monochloramine may be looked upon as an ammonio hypochlorous acid in which the hydroxyl group is replaced by its nitrogen equivalent, the amide group (14). The pK for monochloramine is estimated (15) to be 15 ± 2 in comparison with a pK of 8 for hypochlorous acid. Hence, only in strongly alkaline solutions would monochloramine be expected to be appreciably ionized.



The oxidation potentials of monochloramine have been calculated (15):

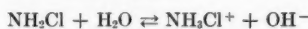


The potential for acid solutions is in agreement with the fact that monochloramine is a stronger oxidizing agent than bromine (for $\text{Br}^- - \text{Br}_2$, $E^{\circ} = -1.09 \text{ v.}$). The potential for alkaline solutions is in agreement with the fact that monochloramine is a weaker oxidizing agent than hypochlorite (for $\text{Cl}^- - \text{OCl}^-$, $E_B^{\circ} = -0.89 \text{ v.}$).

The kinetics of formation of monochloramine from ammonia and hypochlorous acid have been investigated by Weil and Morris (16) who find the reaction to be second order in accordance with the equation:



These authors (17) also studied the base strength of monochloramine and propose an equilibrium constant of 1×10^{-15} for the reaction:



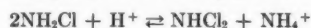
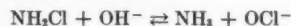
By comparison, the value for ammonia is 1.8×10^{-5} .

A reaction more intimately connected with the Raschig synthesis is the equilibrium:



Corbett, Metcalf, and Soper (18) used a spectrophotometric method to determine the equilibrium constant for this reaction and arrived at a value of 1.6×10^{-3} . This means that only in very strongly basic solutions does monochloramine decompose into ammonia and

hypochlorite ion. These authors (18) also confirmed the earlier work of Chapin (19) who showed that the products of the reaction between ammonia and hypochlorite depend upon the pH of the solution. Below a pH of 3, nitrogen trichloride is formed; between a pH of 3 and 5, dichloramine is obtained; and above a pH of 8, monochloramine is produced. These represent, of course, the principal products formed in each pH region. There is an equilibrium between mono- and dichloramine in the range of pH values of from 5 to 8 and a similar equilibrium between nitrogen trichloride and dichloramine near a pH of 3.

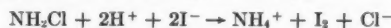


Monochloramine solutions are difficult to preserve for extended periods, the decomposition products being dependent upon the pH of the solution.

ANALYSIS

Three common methods are usually employed for the analysis of monochloramine solutions: (1) iodimetry, (2) colorimetry, and (3) spectrophotometry. The first two procedures are based upon the oxidizing character of monochloramine, while the latter method depends upon the physical constitution of the molecule.

The first method of analysis uses the reaction between monochloramine and iodide ion in acid solution to generate iodine, which is then titrated with thiosulfate. The reaction proceeds according to the equation:



Best results are obtained if the monochloramine solution is introduced below the surface of the acidified iodide solution, to decrease loss of iodine by volatilization.

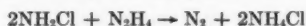
The second method for the analysis of monochloramine is the so-called Palin test (20) in which an instantaneous red color develops when monochloramine, in a phosphate buffer of pH 6.8, is mixed with iodide ion and *p*-aminodimethylaniline. The color fades rapidly, and standard conditions must be observed for consistent results. In a more recent method Palin (21) employs a solution of neutral *o*-tolidine. A blue color appears in the presence of monochloramine after the addition of iodide ion, the blue color then being titrated with ferrous ammonium sulfate.

The third procedure for the determination of monochloramine is dependent upon the characteristic absorption band of this substance at 2430 \AA ., $E = 458$. Recent studies (22) reveal that over the pH range 9–11 monochloramine obeys Beer's law and can be determined in concentrations as low as $10^{-4} M$.

REACTIONS

A number of the reactions of monochloramine have been investigated in some detail. One of the most important reactions, from a commercial point of view, is that between monochloramine and ammonia to form hydrazine (see equation in introduction). It has

been found, however, that hydrazine and monochloramine react according to the equation:



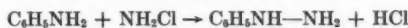
In order to realize substantial yields of hydrazine from the ammonia-monochloramine reaction it is necessary to decrease this yield-reducing reaction between the unreacted monochloramine and the hydrazine that is formed. Since traces of heavy-metal cations, especially copper, have been found to have a marked catalytic effect on the monochloramine-hydrazine reaction (23), the addition of gelatin to the synthesis solutions serves to chelate the undesirable cations and thus permits excellent yields of hydrazine.

Sisler and co-workers (24, 25) have investigated the monochloramine-ammonia reaction in liquid ammonia and in pure water.

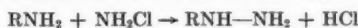


In the former solvent at 100°, yields of hydrazine in excess of 80 per cent of theoretical (based on monochloramine) are obtained for a mole ratio $\text{NH}_3/\text{NH}_2\text{Cl}$ of approximately 400. Using pure water as the solvent these workers have shown that monochloramine and ammonia yield hydrazine in excess of 80 per cent of theoretical, but that the over-all yield is dependent upon the monochloramine concentration.

Raschig (26) reported that phenylhydrazine results when aniline and monochloramine react:



Audrieth and Diamond (27) have demonstrated that monochloramine will react with various primary alkyl amines in basic solution to form the corresponding N-substituted hydrazines, isolated as hydrogen sulfates.



It is interesting to note that, in contrast, monochloramine reacts with certain amino acids at pH 8 to form the corresponding N-chloro derivatives (13). This reaction has been observed with alanine, glycylglycylglycine, and tyrosine, the products being identified spectrophotometrically.



McCoy (28) has presented evidence for the presence of hydroxylamine as an intermediate in the decomposition of monochloramine by hydroxide ion.



The presence of hydroxylamine was demonstrated by the isolation of cyclohexanone oxime.

Monochloramine reacts with certain aldehydes to form solid organic derivatives, ald-chloramines, of the general formula $\text{RCH}=\text{NCl}$ (29).



These crystalline compounds of well defined melting points may be used to establish the presence of macro amounts of monochloramine.

SUMMARY

Some of the physical and chemical properties of monochloramine have been presented. The usefulness of this highly reactive molecule in water purification and in hydrazine synthesis serves to illustrate that monochloramine can no longer be looked upon as a laboratory curiosity.

ACKNOWLEDGMENT

The authors are grateful to Professors L. F. Audrieth and R. S. Ingols for generous discussions and helpful suggestions.

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Proceedings of the

PACIFIC SOUTHWEST ASSOCIATION OF CHEMISTRY TEACHERS

● THE DISCOVERY OF INSULIN¹

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BEFORE the discovery of insulin, diabetes was considered one of the most dreaded and fatal diseases known. It has been estimated that there are two million actual or potential cases of diabetes in the United States alone. If there had been no insulin available, these diabetic persons would have been doomed to die. Some of the symptoms of this disease are: thirst, craving of sweets or sugars, hunger, the passage of large quantities of urine, loss of weight and strength, intense itching of the skin, skin eruptions such as boils and carbuncles, ulcers, sores, extreme fatigue, poor vision, development of hypertension, and eventually death. In essence, diabetes is primarily a disease concerned with faulty sugar metabolism.

Diabetes is not a new disease. It has been recognized, described, and named since the beginning of the Christian era. It is not limited to any one country but has been reported to occur among people of all nations.

A study of the causes of diabetes has been made by numerous investigators. Heredity, obesity, mental shock, and endocrine imbalance are the chief causative factors.

HISTORICAL

Although diabetes has been recorded as a chronic disease for some 2000 years, its relation to faulty sugar metabolism was not recognized until 1675 when Thomas Willis, an English physician, observed that the urine of a diabetic was sweet. Another 100 years passed by before Mathew Dobson (1776) proved by fermentation that the sweet taste of the diabetic urine was due to sugar. The true nature of this sugar was not recognized until Chevreul, a French scientist, identified it as glucose (fruit sugar).

Shortly after Willis reported his famous discovery, Brunner, in Germany, suggested that the pancreas was connected with the metabolism of fats and carbohydrates. In 1682 he attempted the removal of the pancreas of the experimental animal. He concluded that the animal suffered no ill health. In other words, it was his opinion that the pancreas was a useless organ of the body. In 1796 John Rollo initiated the treat-

ment of diabetics by diets that consisted of food of animal origin and vegetables alone. Thus, Rollo was aware of the fact that the diabetic was unable to metabolize properly the carbohydrate in his food.

The origin of urinary sugar in the diabetic became a subject of considerable interest to the scientists of the nineteenth century, for little was known about the pathways of sugars found in the diet and the manner in which they were disposed of by the animal system. The intriguing aspect of this problem was: Why does the nondiabetic show no urinary sugar, as does the diabetic?

This question was not answered until 1835 when Ambrosiani, an Italian scientist, discovered that the blood of the diabetic had a much higher sugar content than that of the nondiabetic, and that his high blood sugar (hyperglycemia) was the cause of glycosuria. This discovery was indeed as important as that of Willis in 1675. Subsequent developments followed with greater rapidity as the etiology of this fatal disease was revealed. In 1843 Claude Bernard, one of the most famous French physiologists and physicians of the past century, explained the origin of blood sugar by his discovery of glycogen. Bernard's theory was that the sugar of one's diet is first digested and then transported by the circulatory system into the liver and muscles, where it is converted into glycogen and stored in these organs as reserve energy. He further produced experimentally a certain type of diabetes termed "Piqure Diabetes."

In 1869 Langerhans made histological and physiological studies of the pancreas and discovered the presence of certain cells in this important organ which he carefully described. These cells became known as "islands of Langerhans." At that time, Langerhans' discovery was considered of mere academic interest, as no particular significance was ascribed to these cells. Numerous histologists and anatomists confirmed Langerhans' findings and classified these cells according to structure and shape. The islands of Langerhans are found in abundance in the human pancreas, to the extent of one and one-half million cells.

One of the greatest discoveries of the nineteenth century, which stands out as a memorable achievement in

¹ Presented before the PSACT at Santa Barbara, February 12, 1955.

medicine, took place in Strassburg, Germany, in 1889. Mehring and Minkowski extirpated the pancreas of an experimental animal and produced experimental diabetes. Although these two scientists were at that time interested in whether or not a certain fat "lipanin" could be absorbed in the absence of pancreatic secretions, they were quick enough to recognize the significance of the development of diabetes following total removal of the pancreas of an animal. Their discovery was minimized by numerous critics who stated that it was sheer luck. Upon hearing of such stupid remarks, Pasteur made his famous remark: "Fortune favors the mind that is prepared."

Minkowski continued his research in the field of experimental diabetes and showed that the feeding of glucose to a depancreatized animal resulted in its total excretion. In other words, the sugar fed was not metabolized by the diabetic animal.

For more than 30 years following the discovery by Mehring and Minkowski of the relationship of the pancreas to diabetes, scientists throughout the world worked feverishly on the pancreas. It was logically assumed that locked therein was a substance that would give life and hope to the diabetic. The islands of Langerhans were considered to be the site of this unknown substance. In 1907 Zulzer published a report that he had successfully obtained an extract of the pancreas that lowered the blood sugar of several of his diabetic patients. Unfortunately his preparation was too toxic and others could not confirm his findings.

There were numerous obstacles in the paths of investigators who attempted the isolation of this elusive hormone of the pancreas. Among these are the tryptic enzymes which we now know are capable of destroying the biologic potency of insulin protein almost instantaneously. Little was known then about this specific antagonism. Thus, time and again experiment after experiment resulted in failure to produce a potent preparation.

In 1909 Ibrahim made an interesting observation that was partly responsible for the discovery of insulin. He reported that the pancreas of fetal calves was devoid of proteolytic enzymes up to about the fourth month. In 1911 Carlson and Drennan confirmed these findings. Little attention was given to this important discovery until a decade later when Banting and Best achieved the isolation of insulin.

DISCOVERY OF INSULIN

Frederick Banting, M.D., a veteran of World War I, had little desire to practice medicine upon his return to a civilian life. He spent a considerable time reviewing the literature on diabetes and familiarizing himself with the investigative work of Willis, Ambrosiani, Chevreul, Bernard, and Mehring and Minkowski. He was firmly convinced that the pancreas did contain a hormone that could metabolize sugar and relieve diabetic symptoms, not only in the experimental animal, but in man. He was unquestionably aware of

the unsuccessful attempts of his predecessors and of the opinion of well known scientists that the anti-diabetic hormone of the pancreas was a mirage. He discarded plan after plan, until one day he came across the observations of Ibrahim and of Carlson and Drennan. He carefully reread these papers and noted that, whereas the pancreas of fetal calves were devoid of proteolytic enzymes, the islands of Langerhans were well developed. This was the impetus he needed for the realization of his dream. He mapped out a plan but he had no laboratory facilities to carry out his project. He approached numerous institutions who turned him down, ridiculing his plan and ideas. Finally he called on Professor McLeod, head of the department of physiology at the University of Toronto. McLeod had no prejudices and carefully listened to Banting's enthusiasm. Banting's confidence of success was contagious and McLeod did not hesitate to offer him adequate facilities in his own laboratory. Two of McLeod's students, Best and Noble, were available and, at the toss of a coin, Best won.

Banting and Best proceeded with their research under the direction of McLeod. Their first series of experiments consisted of ligating the pancreatic duct of several dogs, and these animals were carefully nourished for several weeks. During that time the pancreatic tissue degenerated, leaving the islands of Langerhans intact. Thereupon the degenerated pancreas was quickly removed, minced, and extracted with Ringer's solution. The clear extract was separated and carefully tested by injection into depancreatized animals. Prompt reduction of the elevated blood sugar ensued, along with the disappearance of glycosuria. Thus, for the first time in history, the active antidiabetic principle of the pancreas was realized. It was called "insulin." The year was 1921.

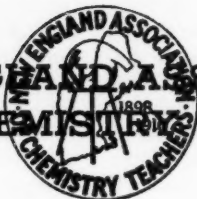
Banting and Best's method for the isolation of insulin was not practical, and as neither McLeod nor Banting nor Best was a biochemist, Collip of Montreal was asked to collaborate in a search for a practical method for the preparation of this hormone. An outline of Collip's method is: Immediately after cattle are slaughtered, their fresh pancreas is minced and extracted with 80 per cent alcohol. The alcoholic extract is recovered, filtered, and its alcohol concentration increased to 90 per cent and refrigerated, whereupon the insulin protein is precipitated. The precipitate is recovered and dissolved in water by the addition of dilute hydrochloric acid.

Banting and Best selected the name "insulin" for the active principle of their preparation. This name had previously been proposed by two independent investigators, DeMeyer in France and Schafer in this country, who firmly believed in the existence of an internal secretion of the pancreas, but who had not been successful in their attempts to isolate it.

Thus, the discovery of insulin by Banting and Best in 1921 is considered to be one of the greatest achievements in the annals of modern medicine.

Report of the

NEW ENGLAND ASSOCIATION
OF CHEMISTRY TEACHERS



● **TRENDS IN HIGH-SCHOOL CHEMISTRY¹**

DOROTHY W. GIFFORD

Lincoln School, Providence, Rhode Island

IN DISCUSSING current trends in high-school chemistry it is well to take a backward look in order to see more clearly the general direction in which we seem to be heading. I must admit that my backward glance has been rather nostalgic, for, somehow, the problems which I faced in the first of my teaching years appear relatively simple now. I remember that I used the current edition of Black and Conant (and a fine book it was), and that I began with the first page on the first day of school and proceeded to march straight through to the last word on the last page. From the accompanying laboratory manual we did 35 or 40 experiments. I can remember getting a little nervous as the last week in May drew near and found alcohols and esters (or the extraction of lead or mercury from their ores) still undiscussed, but it never occurred to me that it was possible to give a respectable course if it left out anything in the book. I recall vividly (and the experience was something like a sudden clap of thunder on a deceptively serene summer's day) the first inkling that I had that times were about to change. In June, 1935, I sent up for the College Entrance Examination in chemistry an unusually able group of candidates. They could do all sorts of problems, write and balance equations for numberless reactions, recite commercial processes flawlessly, and draw diagrams of blast furnaces and the like which would have graced any text. But they came back from the examination in what is commonly termed a "tizzy," for the examiners had seen fit to ask things which were not "in the book." Every one of the straightforward questions included a brainteaser as a sort of bonus. To a request for a diagram and explanation of the blast furnace had been appended the question, "What would happen if steam were accidentally introduced into the furnace?" To the Solvay process had been added this bombshell: "Why is potassium carbonate not prepared in the same manner?" For the first time I

¹ Presented at the dedication of the Newcomb Cleveland Hall and the Chemistry Laboratory, Mt. Holyoke College, South Hadley, Mass., April 23, 1955.

acknowledged that "getting through the book" was not real college-preparatory teaching.

THINKING VERSUS MEMORIZING

There is a definite change taking place in the content of the college-preparatory course in chemistry which is being offered today, a change brought about largely by two factors. When students who have been getting A's in high-school courses go to college and get C's and D's in their freshman chemistry courses, when chemistry departments put into the same course those who offer an entrance unit in chemistry and those who do not, when some college professors say frankly that they prefer students who have had no secondary-school training in chemistry, then it is time for the preparatory teacher to read the handwriting on the wall. And this those of us who are teaching strictly college-preparatory courses have tried to do. We have learned that the freshman course in chemistry offers little hope for the student who has excelled simply through the memorization of masses of facts, that unless he can use those facts in new and different situations he is doomed to grades of C and lower. A second factor which is working very strongly at the present time to change the sort of course which we teach is the achievement test given in chemistry by the College Entrance Examination Board. Most of us affirm with vigor that we prepare for college and not for college boards, but the fact remains that the student must be *admitted* to college before the excellence of our preparation can make itself known. Though we hate to admit it, from the first day of school in September the March achievement tests have a nasty way of insinuating themselves into our classrooms. I try very hard not to mention them, but I find myself wording questions and devising situations which I think will resemble them. I do not know how much you know about these tests, but at the risk of boring you, I should like to discuss them briefly. They are becoming less and less factual, and they are aimed more and more at selecting the student who can "think

chemically." While all the questions are objective in nature, they can still do a pretty good job. One sort of question gives a description of an experiment followed by a number of statements. The description is to be studied and then each statement is to be classified under one of four categories: (1) The statement is true and an expected observation; (2) The statement is true and a justified conclusion; (3) The statement is true but is not related to the experiment; (4) The statement is contradicted by established facts or principles. Another type of question consists of an assertion followed by a reason. The student has to decide whether the assertion and reason are both true and related as cause and effect; whether both are true but are not related; whether the assertion is true but the reason is false; whether the reason is true but the assertion is false; whether both are false. I think all will agree that questions of this sort are a far cry from the old "describe the commercial preparation of aluminum" type.

What kind of course can be given which will develop to the fullest any latent ability to cope with problems like this? And what sort of course can be given which will send to college students with the intellectual vigor and curiosity which will enable them to master with some degree of self-respect the work which is demanded of them in their freshman course in chemistry? The secondary-school teacher must somewhere find the courage to fling aside preconceived notions and outmoded syllabi. He must get over the idea that it is a mortal sin to send to college a student who knows nothing of metallurgy. He must dare to teach a course that puts first things first, and lets the descriptive details take their proper place. And this sort of teaching is actually going on in a number of secondary schools. In my own classes just as soon as preliminaries like the scientific method and terms like matter, element, compound, mixture, and concepts like atoms, gram-atoms, molecules, moles, and physical and chemical changes have been introduced, we go at once into the study of the periodic classification of the elements. This is followed by a consideration of atomic structure and of its relation to valence. Then we discuss symbols, formulas, and the writing and balancing of chemical equations. Then, and then only, do we begin descriptive chemistry which from then on is linked as closely as possible with the periodic chart. This takes an enormous amount of time, and every year I have what is practically a nervous breakdown when December comes along and I have still done nothing which is very orthodox chemistry. I had thought that this type of course was my own personal possession until a short time ago when I was talking with a friend who teaches in one of the extremely good preparatory schools in the vicinity of Boston, and found that his course is basically the same as mine. I think that each of us felt a good deal of relief in finding that each was having the courage of the other's convictions. I might add that I know of no textbook written for secondary schools which is built around a course of study such as I have outlined.

Changes in laboratory work are taking place. Some of them have a good deal to be said for them, and others are unfortunate. The good teacher has always avoided the "cook book" type of laboratory procedure, but in the days when a required number of laboratory experiments had to be done, the inquiring student had little opportunity for the exploration of possibilities which were suggested to him by the work which he did while "following the recipe." Now that we no longer feel the pressure of meeting a requirement in regard to the number of experiments to be completed, many of us are encouraging the student to investigate interesting by-paths during his regularly scheduled laboratory periods. If I find a girl who has an interest in the recovery of by-products, I allow her a good deal of time for their isolation. If the perfectionist wishes to try a quantitative experiment again in an endeavor to get better results, I encourage her to do so, providing she can make a definite statement in regard to the improvement in technique at which she is aiming. Quantitative experiments are necessarily time consuming, but I believe that they teach more, if the proper interpretation of results is demanded, than the more descriptive work. From such conversations as I have had with my colleagues, I have come to believe that there is a steadily growing emphasis on this sort of laboratory work. There is also a growing tendency to get away from ready-made laboratory situations as we attempt to introduce into the laboratory something which will demand ability to meet an emergency. For instance, in the experiment done to find the weight of a liter of oxygen at standard temperature and pressure, I always use collecting bottles of different sizes. At least one student will get a bottle which is so big that she cannot possibly equalize the water levels inside and out. The girl who thinks herself out of that situation has learned something about the gas laws which it will take her a long time to forget!

There are many of us who deplore (and are doubtless dated by this reaction) the increasing tendency toward the workbook type of laboratory report in which the student merely fills in blanks in response to what are usually pretty leading questions. The old-fashioned written laboratory report seems to be on its way out. The average teacher should not be too strongly blamed for this trend, for he teaches too many pupils too many hours per week to have time left for the long job of careful correction of such papers.

Before I leave this discussion of laboratory work, I should speak of an outgrowth of laboratory experiences as evidenced in science-fair exhibits. Anyone who has had any intimate contact with such fairs cannot help being impressed with the variety and individuality of the exhibits and with the enormous amount of work which has gone into them. At our recent fair in Rhode Island there was a demonstration of the qualitative analysis by chromatography of citrus fruit juices that I would have been proud to have done myself. A few years ago a student of one of the finest teachers whom I know demonstrated, by making his own alloys, that the

statement in a certain widely used text in regard to the composition of the variously colored forms of gold was not true. Obviously such work is the outgrowth of classroom experience and much of it is carried on in the school laboratories.

BETTER QUESTIONS

I think that we are learning, too, to ask our students better questions. I do not know how long it has been since I have asked a question like, "Describe the commercial preparation of hydrogen," or "Diagram and explain the commercial preparation of aluminum." Instead, these are the sorts of questions with which I confront my girls. After they have studied the reactions of water with oxides, I ask for the equation for the probable reaction of cesium oxide with water. A quiz on the halogens would deal with how free astatine might be prepared; with how its hydrogen compound might be prepared from astatides; with what products might be obtained when hydrogen astatide reacts with concentrated sulfuric acid; with how the test for the astatide ion would be like and would differ from that for the chloride ion. After the study of the naming of ternary acids and salts I gave this question: " H_3XO_3 is the formula for 'Unknownic acid.' Write the formula(s) for and name its rubidium salt(s). What would be the name of K_2XO_4 ? $FeOX$? $Mg_3(XO_2)_2$? H_3OX ?" And here is one last question of this sort which I found added quite a fillip to my class just before midyears. "If you were to be guillotined for giving a wrong answer and had to answer one of these two questions, which one would you choose and why? (1) Describe the reaction of beryllium with cold water. (2) Describe the reaction of rubidium with cold water."

If I were to summarize, then, the curriculum changes which seem to me to be taking place—or if they are not, should be—I should say that we are gradually coming to teach less factual material, but that we are demanding in its place a greater understanding of the chemical principles illustrated by such factual material; that we are trying to make the student use the facts and principles which he knows in meeting new situations in an intelligent fashion; that we are trying to make his laboratory work less mechanical, more thoughtful, more honest, and more intellectual.

TODAY'S STUDENT

All of this promises a course of far greater difficulty than the old-fashioned memory type. What about the students who are coming along to take such courses? Is there any trend discernible in them? For those of us who are teaching in the strictly college-preparatory school, the answer is not too difficult to give. Boys and girls are just as bright as they have always been. However, many of them seem to me to use the tools of learning less well. They spell poorly; they seem less able to express themselves clearly, fluently, and grammatically; their arithmetic is less sure. Almost all of them show a greater reluctance to do the hum-drum memory work which is required in any academic subject. All of

them seem more "beset by the world" than they were even five years ago. They cannot seem to give the academic world their wholehearted attention. One would like to blame the movies, the radio, and the television which do so much of their thinking for them. But their difficulty is different from the American tendency of using ready-made thoughts like cake mixes; there seems to me to be a genuine unrest and uncertainty which makes their school life seem less important than it used to. Boys must face the fact that in all probability their academic careers will be interrupted by military service. Girls, I believe, are being influenced by the growing acceptance of early marriages and the necessity of marrying early if they are going to marry at all. Such uncertainties cannot help but make academic careers seem less important. If this is a dark picture, it is lightened by a saving attribute which makes the present generation much more interesting to teach than were the students of ten years ago. There has been and is a steady growth, at least on the part of the young people with whom I come in contact, in enthusiasm for using the mind in a reasoning process. A class which slogs along with an ordinary memory assignment goes by leaps and bounds when being led into new concepts by deductions drawn from former experiences. My girls love the periodic chart because with it they can reason things out instead of learning them. They rise more readily to the bait of the "thought" question than they did five years ago, and they glory in the sense of power which such successful reasoning gives them. In March the candidates whom I sent up for the achievement test in chemistry complained, not because there were so many thought questions, but rather because there were too few of them. Their general comment was, "Anyone with a memory could have answered some of those questions." The catch seems to be to sell the idea that it is really pretty difficult to do much reasoning unless one is master of a few facts on which to base his deductions.

The teacher in the school which does not emphasize college preparation is confronted by a much more serious problem. With the growing feeling that everyone should finish four years of high school, and with the increasing size of the high-school population, there is more and more tendency toward larger classes which are less carefully sectioned. Thus, in the same group will be found pupils who have no abilities to fit them for four-year college work and students who are extremely able. Increasingly heavy pressure is being brought to bear to water down course content to fit the average student in the course, and the strictly academic approach has to be abandoned in favor of material which has more popular appeal and is more easily mastered. After all, a teacher cannot flunk half of the students in his class and get away with it very long. The larger and more generalized our schools become, the more difficult it is going to be to maintain a strictly academic approach, and to the critic who will say at this point that this is a good tendency, I will answer with the title of an article in the April *Scientific Monthly*: "Wanted:

more ivory towers." We need to consider more seriously the rights of and our responsibility toward the exceptionally gifted child, for he is in danger of being lost in the shuffle, of learning to get by with less than his best, of having his intellectual curiosity stifled by indifference or starved by neglect.

THE TEACHER SHORTAGE

But the most serious trend seems to me to lie in the problems introduced by the teacher shortage. Many of you are doubtless familiar with a pamphlet called, "Critical Years Ahead in Science Teaching"—a pamphlet which summarizes a conference held in August, 1953, at Harvard University to consider nationwide problems facing secondary-school science teaching. Particularly I would remind you of a section which states that at the present time there is an annual demand for 7000 new science teachers and that this number will shortly become 10,000. To meet this need there is a maximum potential of 5000 replacements from new college graduates. Anyone who has tried recently to hire a young science teacher knows the reality of this problem of finding good teachers. My last experience is very vivid in my mind. I recall one candidate who said quite frankly that she did not like the high-school age, but that she would consider such a job until some college made her a satisfactory offer. A second assured me quite solemnly that an efficient teacher could arrange her work so that she would not have any papers to take home to correct. These, obviously, are not the people who should be hired to fill the vacancies in the secondary-school systems. How can we gather into the field of secondary-school teaching young men and women who can fan the flame of intellectual curiosity in the potential scientists in grades 9 to 12? The lure of the long summer vacation is inadequate, for in all honesty we must tell them that their summers will often be spent working at other jobs or in doing graduate study in order to qualify for teaching certificates or to meet other requirements. What about the salary situation? Again we must be discouraging, for we must say that in industry not only will they get a better starting salary, but that all along the line their advancement will be more rapid and their salary increases larger. The customary regular annual salary increase in many of the school systems continues to be what it has been for the last 25 years—\$100. What industry would think of offering today to a valued employee a raise of this sort which comes to 50 cents per day! If the new graduate is considering teaching in the independent school, which some of us believe to be the great stronghold of academic freedom in the secondary-school system, the salary picture which we must paint is even more gloomy. Unless he has the good fortune to find a job in one of the few heavily endowed schools, the teacher must expect to start at a lower salary, have less rapid increases, rise to a lower maximum, and finally retire with a much more inadequate pension. And what of working conditions? The teacher in the average public high school must expect to undertake a

heavy classroom schedule. His classes will usually be large, the laboratory is often inadequate for the size of the group, and the time allowed for laboratory work is increasingly encroached upon. I truly believe that the remark which is heard most frequently at meetings of science teachers is, "I have to do the best that I can under the circumstances." In the average independent school the classes will be smaller and the arrangements for laboratory work will be more adequate, but the teacher, unless he is working in one of the very large or heavily endowed institutions, must expect to teach two, three, or even four different subjects. He carries a heavy schedule, not quite so bad usually as that of the public-school teacher, but he must assume responsibility as well for a good many varied extracurricular activities. His school year is shorter, but he works harder and puts in longer hours than his public-school colleague.

While the good teacher welcomes the opportunity for individual work which the small independent-school classes afford, we should not overlook the fact that such individual work is time consuming. What chance has he of that eventual public recognition of the excellence of his work which can be such balm to his weary soul? Let me ask you a series of questions. How many of you ever heard of a teacher's being made an honorary member of Phi Beta Kappa because of the brilliance of his science teaching in high school? How many teachers do you know who have been made honorary members of Sigma Xi in recognition of the debt which research owes to them because of students who received their initial inspiration under their tutelage? How many colleges do you know which have given honorary degrees to their graduates who teach in secondary schools in recognition of their contribution to education? Just as attempts are being made to do something about the salary situation, so there are certain definite attempts being made to give public recognition to the contribution of the high-school science teacher to the society in which he lives. In October, 1952, at a convocation held at Mount Holyoke, in connection with a conference on Science and Industry, one of the alumnae who received a special citation was a secondary-school teacher of biology. Each year for the past four years the Brown University chapter of Sigma Xi has made a cash award to "an outstanding teacher of science in Rhode Island." At the time of this award a dinner is given at which a dozen other outstanding teachers of science are the guests of the Providence Journal Company. Last December at a joint meeting of the New England Association of Chemistry Teachers, The Eastern Association of Physics Teachers, and the New England Biological Association, the American Academy of Arts and Sciences gave five cash awards, known as the Elizabeth Thompson awards, to outstanding teachers of science in New England. At present the American Association for the Advancement of Science is completing plans for a number of similar annual awards. No teacher works for the sake of public recognition, but I doubt if a little glory will hurt any of us much, and these are encouraging signs that

high-school teachers of worth will be recognized and duly honored.

SALESMANSHIP NEEDED

I am afraid that the picture which I have been painting is not a very attractive one, but, although I am sure that low salaries and poor teaching conditions have had something to do with the present teacher shortage, I am certain that it stems from something more vital, and that is the failure of teachers to sell the profession. I get so annoyed when I hear a group of teachers discussing nothing but their troubles. We have been worrying so much over our inadequate salaries and the other difficulties under which we work, and we have made our trials and tribulations so public that we have given the impression that we teach as a last resort rather than from having made a wise and deliberate choice. We ourselves ought to recognize that practically every one of us could get another type of job if he really wished to do so, and that we are in a field in which, for one reason or another, we have chosen to stay. My grandmother was a teacher; my mother was a teacher. I was brought up to believe that teaching is a wonderful profession. My mother sold teaching to me. For as long ago as I can remember, I have never really dreamed of doing anything else. Two of my secondary-school teachers sold teaching to me. One of them taught me English and the other introduced me to the science of chemistry. Obtuse as I was, I sensed in the lives of these two people something which made me wish to teach. Then I came to Mount Holyoke, and here I found more people who were aflame with the joy of imparting information and stimulating intellectual integrity and enthusiasm. No student of my generation could work in the biological sciences and not realize that something besides dollars and cents made life worth living for Miss Turner, Miss Morgan, Miss Addams, and Miss Smith. Every day in the physical sciences made one realize that Miss Carr, Miss Laird, Miss Hahn, Miss Allen, Miss Stevenson, and Miss Sherrill might be brilliant scientists, but that they were first of all great teachers who rejoiced more at a sign of independent thinking on the part of a student than in the successful completion of a piece of research. There are a good many Mount Holyoke graduates all over the world who are teaching science, and if we are any good, I believe that our inspiration has come by a sort of apostolic succession from these extraordinary women who sold us the profession, whose obviously rich and full lives taught us where real satisfaction lies. I welcome this opportunity of expressing publicly for myself and for my fellow alumnae who teach science the boundless gratitude which we feel for the vigor of approach and the excitement in learning which they

transmitted to us and which we, in turn, should like to pass on to our own students.

And does this appear to be rather remote from trends in high-school chemistry? It seems to me very intimately associated with the subject, for the scarcity of science teachers in high school is a stark reality. In the years directly ahead (next year, not five years from now) we must find more real teachers or we must teach poorer chemistry. There is no alternative. The public is awakening to the salary situation, new and better schools are being and will be built, but nothing can sell the teaching profession except the teacher himself, and it is time that we took an objective look at ourselves. When our faces reflect the intellectual and spiritual satisfaction which life brings to the real teacher, we shall find in our classrooms students who will feel that teaching offers the greatest of rewards and the keenest of satisfactions. Then the teacher shortage will be at least partially solved, for there are in every generation, thank heaven, people who are more interested in intangibles than in the goods of this world.

It is always dangerous to indulge in prophecy whether in regard to the weather or to education, yet I venture to predict that in the future we shall be sending to college students who know less descriptive chemistry but will be better able to use what they do know, who will have a better command of laboratory techniques and more understanding of the significance of quantitative experimental work, who will expect to be asked to use their heads (and many of them will actually enjoy it). These I think you will all agree sound like highly desirable material, and that is what we aim to develop. But I see on the horizon clouds which threaten this rosy picture, and they are black and ominous. I see the overcrowded conditions in our science laboratories; I see poor sectioning of students; I see too heavy schedules which make adequate preparation and individual attention almost impossible; I see last of all the cruel and relentless fact that there simply are not enough teachers to fill the need right now, let alone five years from now, and I cannot help wondering what is going to happen to our beautiful plans for better teaching of better chemistry courses.

I think that I shall end these remarks with what I shall call the chemistry teacher's version of the last verse of the thirteenth chapter of first Corinthians. "And now abideth *faith* in the educational value of the subject which we are trying to teach and in the intellectual vigor and integrity of our students, *hope* that our material difficulties will be solved and that we shall be able to give the sort of course which our faith demands, *love* of the jobs which we have deliberately chosen and in which we wisely and deliberately remain, these three; and the greatest of these is love."

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Recent Books

● OUTLINES OF ENZYME CHEMISTRY

J. B. Neilands, Assistant Professor of Biochemistry, and Paul K. Stumpf, Associate Professor of Plant Biochemistry, University of California, Berkeley. John Wiley & Sons, Inc., New York, 1955. x + 315 pp. 73 figs. 39 tables. 15.5 × 23.5 cm. \$6.50.

STARTING on a level understandable to graduate students who have had a thorough grounding in chemistry, biochemistry, and physiology, and advancing to the level of the specialist, this book discusses in 24 chapters all aspects of enzyme chemistry. The history of the field is described first. Equilibria and ionization, reaction rates, effect of external conditions and inhibitors, the mechanism of enzymatic catalysis and its specificity are presented in physicochemical terms. The isolation, purification, characterization, and classification of enzymes and co-factors form a bridge to more biochemical considerations of the many facets of metabolic patterns in which enzymes are involved. In this part of the book, glycolysis, the carbohydrate cycles, oxidative phosphorylation, and fatty-acid oxidation are the main chapters. The book closes with a unique discussion of enzyme synthesis by the cell. This chapter, written by Roger Y. Stanier, of the University of California, calls attention to complex phenomena too often disregarded by biochemists who have not worked with bacterial enzymes themselves. One is impressed with the relative newness of the field; few references are more than five years old, and many are of most recent date. The book is attractively printed; the many formula schemes add to the understanding, and the photographs of outstanding enzyme chemists add to the enjoyment of this excellent monograph.

ALFRED BURGER

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● PHYSICAL CHEMISTRY MADE PLAIN

J. H. Mandelberg. Cleaver-Hume Press, Ltd., London, 1952. viii + 287 pp. 14.5 × 22 cm. 15s.

VAST numbers of students of chemistry would welcome a book which could "make plain" physical chemistry. Unfortunately for their hopes, this little book has much too big a title. It is written by an industrial chemist who is, according to his preface, "a chronic and incurable non-mathematician." He points out that experts, who are the usual authors of textbooks, are sometimes "out of touch with the elementary difficulties of the expert, because they have never themselves experienced these difficulties and can hardly imagine anything so stupid."

The book is written for the "intermediate" level—a little beyond an advanced freshman course, but below that of the usual physical chemistry course in this country. Brief outlines of principles are given, but most of the book consists of problems worked out in considerable detail. Although many of these are of the type which involve direct substitution in familiar equations, there are a number which involve more complex reasoning, and their study can be helpful.

One error noted by this reviewer is the statement that three sets of data are needed to evaluate the van der Waals constants a and b , since "there will be three unknowns, a , b , and the product ab ." In spite of advice in the appendix about precision, the

author sometimes gives three or even four significant figures in answers to problems where only two are given in the data.

The discussion of principles is necessarily too abbreviated to be of much value, but some students may profit by studying the solutions to the problems, and instructors may find in the book some useful suggestions.

WILLIAM E. CADBURY, JR.

Haverford College
Haverford, Pennsylvania

● ORGANIC REACTIONS. VOLUME VIII

Roger Adams, University of Illinois, Editor-in-Chief. John Wiley & Sons, Inc., New York, 1954. viii + 437 pp. 59 tables. 15.5 × 23.5 cm. \$12.

VOLUME VIII of this well known series presents another significant contribution to the literature of organic chemistry. The high standards for excellence of the previous volumes have been maintained. The breadth of the field of organic chemistry is well illustrated by the fact that the reactions discussed in Volume VIII are of no less importance than those covered in earlier volumes.

The chapters included in this volume are: "Catalytic hydrogenation of esters to alcohols," by Adkins (27 pp.); "The synthesis of ketones from acid halides and organometallic compounds of magnesium, zinc, and cadmium," by Shirley (30 pp.); "The acylation of ketones to form β -diketones or β -keto aldehydes," by Hauser, Swamer, and Adams (137 pp.); "The Sommelet reaction," by Angyal (20 pp.); "The synthesis of aldehydes from carboxylic acids," by Mossetig (39 pp.); "The metalation reaction with organolithium compounds," by Gilman and Morton (46 pp.); " β -Lactones," by Zaugg (58 pp.); and "The reaction of diazomethane and its derivatives with aldehydes and ketones," by Gutsche (65 pp.).

The literature is reviewed through 1949 for the hydrogenation of esters, through mid-1950 for the synthesis of ketones, and only through 1948 for the acylation of ketones. In the remaining chapters, the literature is covered through 1952.

The editors and authors are to be congratulated for the quality and usefulness of this work. Organic chemists will welcome this newest addition to an indispensable series.

ROBERT K. INGHAM

OHIO UNIVERSITY
ATHENS, OHIO

● SUPERFLUIDS. VOLUME II: MACROSCOPIC THEORY OF SUPERFLUID HELIUM

Fritz London, late Professor of Theoretical Chemistry, Duke University. John Wiley & Sons, Inc., New York, 1954. xvi + 217 pp. 56 figs. 6 tables. 15.5 × 24 cm. \$8.

THIS posthumous book by Professor London maintains the high standard which we have learned to expect from him. The high price per page reflects the expense of setting mathematical equations, but reflects even more the author's unwillingness to tolerate less than his best, even when the type has already been set.

This book is a companion to Volume I, "Macroscopic Theory of Superconductivity." A two-fluid mechanism has been employed to explain superfluid helium, much as was required for the superconductivity of electrons, in spite of the fact that they obey different statistics. The two types of fluid helium interpenetrate each other and coexist in every small volume of the system. The superfluid state arises from the small mass of helium, the low intermolecular attraction, coupled with the condensation phenomena arising from the degeneracy of Bose-Einstein statistics. London has done an outstanding job in systematizing the knowledge we have of helium, but points out that a more detailed theoretical treatment can only come with new methods for treating the many body problem. Anyone interested in the theory of low-temperature phenomena will not want to be without this exacting but excellent book.

UNIVERSITY OF UTAH
SALT LAKE CITY, UTAH

HENRY EYRING

SILICONES AND THEIR USES

● *Rob Roy McGregor*, Administrative Fellow, Mellon Institute. McGraw-Hill Book Co., Inc., New York, 1954. xv + 302 pp. 15 × 21 cm. \$6.

THE very rapid expansion of the silicones industry during the last decade has been due to the wide variety of uses for these interesting and unusual materials. Today silicones are used in one form or another in almost every industry.

Since the silicones are still relatively new materials which are being used by nonspecialists in diverse applications (which will certainly be expanded), there existed a real need for an extensive treatment of the properties and uses of the silicones, written primarily for the nonspecialist who is a potential or actual user of silicones. The need has been admirably filled by this book.

Dr. McGregor has been intimately associated with the silicones industry from its inception, and has written well on a subject with which he is obviously thoroughly familiar.

The subject matter of the book may be indicated by listing the chapter headings: I, History of Silicones; II, Commercial Silicones; III, Physiological Response to Silicones; IV, Applications of Silicones to Specific Industries and Cost Considerations; V, Chemistry of Silicone Preparation.

In summary, it seems clear that this book can serve excellently as a "practical manual on silicones for engineers, designers, and others who wish to use these products."

PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA

LEO H. SOMMER

A MANUAL OF PAPER CHROMATOGRAPHY AND PAPER ELECTROPHORESIS

● *R. J. Block*, Department of Biochemistry, New York Medical College, *E. L. Durrum*, Department of Pharmacology, Army Medical Service Graduate School, Walter Reed Army Medical Center, and *G. Zweig*, Charles F. Kettering Foundation and Antioch College. Academic Press, Inc., New York, 1955. ix + 484 pp. 85 figs. 104 tables. 15.5 × 23.5 cm. \$8.

THIS book is divided into two parts. The first part (329 pp.) is a revision of the earlier book on paper chromatography by Block, LeStrange, and Zweig. The second part (77 pp.) is contributed by E. L. Durrum, an expert in the field of differential electrical migration in moist paper. Separate bibliographies are provided for each part, but author and subject indexes are for the two parts.

This monograph is the product of specialists in the fields of proteins and amino acids. Written from the specialist's view-

point, it will be most useful to those applying the technique and to those requiring a guide to current investigations. For the practicing chemist, this publication provides an excellent summary of theory, procedures, methods, detection techniques, and various applications. It illustrates the importance of paper chromatography and of electrochromatography as analytical tools in numerous investigations.

The authors' experience is reflected in the large space devoted to investigations of proteins and amino acids. Indeed, the first analytical applications of sorptive paper in these fields are regarded as the beginning of paper chromatography even though one-way, two-way, and radial or circular modifications of the technique had already been employed with plant pigments and with dyes.

Although the numerous modifications of paper chromatography and their applicability in many diverse fields present great difficulties in the preparation of a concise, coherent book, a great quantity of material has now been summarized remarkably well. Certain aspects of the treatment may, however, be brought into question. The definition of chromatography quoted in the first chapter is inexact and equivocal. The historical treatment of electrochromatography as well as of paper chromatography is incomplete. The restriction of theory to partition chromatography is no longer justifiable. Various terms widely employed for paper electrophoresis are not included. There are few basic rules for operation and application of the techniques, and there are few examples of easily reproducible experiments with readily available materials.

In spite of these irksome criticisms, this book is a major contribution to the subject of chromatography. In this rapidly expanding field it provides a bench mark for the survey of further progress.

ARGONNE NATIONAL LABORATORY
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HAROLD H. STRAIN

AMERICAN MEN OF SCIENCE. VOLUME I: PHYSICAL SCIENCES

● Edited by *Jaques Cattell*. Ninth edition. R. R. Bowker Company, New York, 1955. 2180 pp. 20 × 28.5 cm. \$20.

SO GREATLY has the membership of the scientific fraternity increased that some 90,000 names must be included in this ninth edition of a reference book of great value. It will appear in three volumes of which this, the first, contains over 40,000 names of workers in the fields of the physical, mathematical, chemical, and geological sciences. The general policies and format of the earlier editions have been followed.

REAGENT CHEMICALS AND STANDARDS

● *Joseph Rosin*. Third edition. D. Van Nostrand Company, Inc., New York, 1955. x + 561 pp. 16 × 23.5 cm. \$9.50.

THE earlier editions of this work have long been standard items on the shelves of every analytical laboratory. Analytical chemistry has advanced enormously since the last edition (1946), particularly with the development and extension of methods involving spectrophotometry, chromatography, nonaqueous titrations, etc. New reagents and solvents have been introduced, some 45 of which are incorporated in this volume.

TABLES OF INTEGRAL TRANSFORMS. VOLUME 2

● Edited by *A. Erdélyi*. McGraw-Hill Book Company, Inc., New York, 1954. xvi + 451 pp. 16 × 23.5 cm. \$8.

EXTENDS the list of integral transforms from Volume 1, and includes many transcendental functions.



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By Howard Ritter, Miami University, Ohio. Written to accompany the author's *An Introduction to Chemistry*, this manual is also designed for use with other texts. It is intended for a full year's work and is sufficiently flexible to meet the needs of both 3 and 6 hour courses. Every exercise in the manual is a single problem, usually with a single answer. Each experiment is carefully planned to illustrate one or more important principles. The author avoids traditional experiments of a purely

descriptive nature, feeling that these properly belong in the lecture-demonstration part of the course. Nearly all the experiments are quantitative. The manual includes a scheme of qualitative analysis involving 12 cations and essentially all the principles of the classical scheme. Four simple syntheses—one inorganic, two organic, and one biological—are included, and there is an industrially significant exercise in classical quantitative analysis. 1955. 179 pages. \$2.50.

BIOCHEMISTRY: An Introductory Text

By Felix Haurowitz, Indiana University. Here is the first text to treat general biochemistry at an introductory level. It incorporates material on animal, plant, and bacterial biochemistry, stressing the problems that are common to all fields. It provides detailed coverage of the two major developments in biochemistry in recent years—the transfer reactions and energetics. There are also extensive chapters on enzymes and the metabolism of inorganic substances, topics which are frequently subordinated at this level. Though it forms only a part of the text's subject matter, human or medical biochemistry

is not slighted—there is ample material on the body fluids and the human organs and tissues. The book opens with a clear exposition of the basic principles and then builds the subject on this foundation. Throughout the text the chemistry and metabolism of the main organic constituents are treated together rather than separately. A special point is made of clear definitions of the terminology of modern biochemistry. There is useful reference material at the end of each chapter and an ample glossary. 1955. 485 pages. \$6.75.

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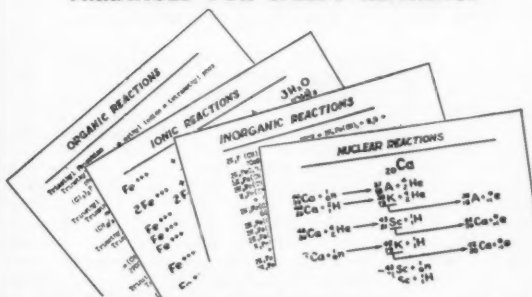
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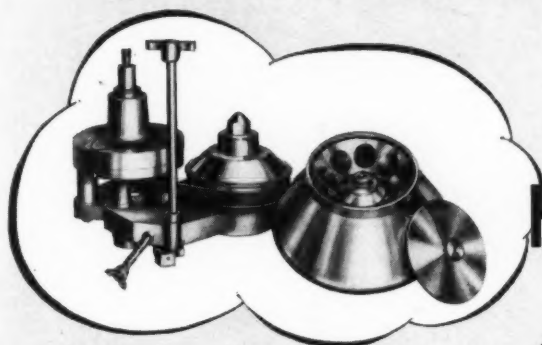
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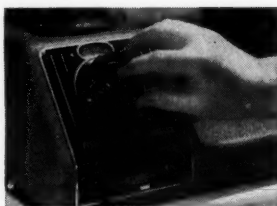
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